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ABSTRACT

This report summarizes the development, history, and operational use of liquid ammonium phosphate and polyphosphate fire retardants since their first use in the early 1960's. Several liquid ammonium polyphosphates were evaluated as long-term forest fire retardants in accordance with Forest Service specifications and test procedures. Retardants were laboratory tested to quantify various physical properties, corrosion potential, and combustion retarding ability, and were drop-tested from aircraft. Performance of products is discussed and recommendations are made relative to meeting current Forest Service specifications and satisfying current and future operational needs.

INTRODUCTION

Since chemicals were first used to combat wildfires many different formulations have been tried. Thickeners were one of the first important additives combined with water to increase its effectiveness. The thickened water adhered to fuels in heavier layers to dissipate more heat than unthickened water. Eventually, chemicals were included in the thickened water to alter the combustion process of the fuel by causing lower production of flammable pyrolysis products. When spoilage and corrosion of some formulations occurred, chemical inhibitors were added. The most effective fire retardant chemical additives were ammonium phosphate (DAP), polyphosphate (APP), pyrophosphate (Pyro), and sulfates (AS). DAP and AS are mixed with water as dry powder-type retardants and APP and Pyro as liquid-type retardants.

As numerous products containing several different chemicals were made available, it became necessary to screen and test formulations before they were accepted by the Federal Government and put on the market for general use. Procedures were written and incorporated into Forest Service specifications to provide a basis for testing, qualifying, GSA purchasing, and retesting products as necessary. All new retardant formulations submitted for USDA Forest Service use now must be tested against requirements in current specifications for dry retardants or for liquid retardants. Final performance evaluation and approval for the Forest Service are given by the Washington Office Division of Fire Management. Many States and other Federal agencies often comply with the evaluations and approval decisions that are based on the Forest Service Specifications.

This report discusses the development history, operational use, and related performance requirements of APP-based forest fire retardants and details their performance when tested and evaluated according to USDA Forest Service Specification 5100-00302a for liquid fire retardants. Most of the formulations discussed contain 10-34-0 ammonium polyphosphate and are referred to as APP solutions. In everyday language, several of these are referred to as liquid concentrates or LC.

Ammonium polyphosphates differ considerably in their composition, but usually contain 20-30 percent polyphosphate (P_3O_8 or greater), 30-50 percent pyrophosphate (P_2O_7), and 20-50 percent orthophosphate (PO_4). Numerous laboratory tests have shown that the effectiveness of ammonium phosphate solutions is related to the amount of active phosphate that is available to alter pyrolysis and combustion reactions. Impurities such as calcium, magnesium, and iron in these solutions can chemically tie up available phosphate and reduce the effectiveness. Most dry ammonium phosphate salts (DAP) and "white acid"- or electric furnace-produced liquid phosphates (APP or Pyro) usually contain few impurities and thus do not significantly reduce the solution effectiveness. "Green acid"-produced dry salts or liquids (currently used APP or LC) however, can contain many impurities and reduce the effectiveness of the solutions by 10 percent or more (on a P_2O_5 equivalence basis). Thus, total phosphate concentration does not necessarily quantitatively relate to "retardant effectiveness." This is shown by data included in this report as well as that on file at the Northern Forest Fire Laboratory, Missoula, Montana.

DEVELOPMENT HISTORY

Several different dry-type ammonium phosphates were evaluated as forest fire retardants both individually and in complex formulations during the late 1960's. Included were several ammonium polyphosphates such as MAPP (monoammonium polyphosphate), 15-60-0, and several long-chain, water-insoluble ammonium polyphosphates that are often used in fire retardant paints. Liquid-type ammonium pyrophosphate (Pyro or 11-37-0) was evaluated and used operationally in the Southeast (Johansen and Crow 1965), but the liquids were not formulated with coloring, corrosion inhibitors, thickening agents, or other additives. This liquid product was not used in the Western States until 1970, apparently because of undesirable physical properties and not because of the effectiveness of the basic chemicals.

During tests in the late 1950's in California (Davis 1959; Davis and others 1961, 1962, 1963; Phillips and Miller 1961), unthickened and thickened ammonium phosphate was dropped from aircraft and applied by ground tankers onto chaparral-type fuel. Although the tests were quite subjective, it was concluded that thickening agents were necessary to improve the drop characteristics and/or to increase retention on fuels, especially for fires spreading through aerial fuels during windy conditions and/or in steep terrain where high aircraft drops were necessary. Viscous products such as Bentonite, Borate, Algin-Gel, Gelgard, Algin-DAP, Pectin-DAP, CMC-DAP, and eventually Phos-Chek and Fire-Trol 100 were developed to improve the drop characteristics of water or retardant solutions.

Meanwhile, in the Southeast States, fire control personnel were successfully dropping Pyro (with no additives) from air tankers with few, if any, apparent delivery problems. This successful use created numerous Pyro advocates who could not understand the lack of interest by western fire control personnel in using this product. Discussions began as to whether coloring, corrosion inhibitors, or other additives were really necessary and led to a controversy over the use of such chemicals.

The proponents of Pyro suggested that the Southeast's fire retardant needs and use levels were comparable to those of the Western States and therefore proposed that the same materials could be used in all regions. However, the amount of use, general practices, type of fuel, type of fire, and topography in the areas where Pyro was being used were considerably different from those in the Western States. For example, the amount of use: for the years 1962 through 1969, the Southern Region of the Forest Service dropped 958,000 gallons of liquid concentrate (Pyro) for an average annual use of about 120,000 gallons (the peak year was 1963 when 288,000 gallons were used). During the same period, the Western Regions (Northern, Rocky Mountain, Southwestern, Intermountain, California, and Pacific Northwest) of the Forest Service dropped 38,945,000 gallons for an average annual use of 4,868,125 gallons. In addition to the retardant used by the Forest Service in the West, the average annual use for the California Division of Forestry and the Bureau of Land Management for this period was 2,863,000 and 846,000 gallons, respectively. Thus, during this 8-year period, the use of Pyro averaged less than 2.5 percent of the retardant used annually by the Forest Service or approximately 1.4 percent of the total retardant use in the West.¹

¹ Data collected, summarized, and reported by individual Regions and agencies. Summary data acquired from conversations with agency personnel is on file at the Northern Forest Fire Laboratory, Missoula, Montana.

Another example is general use practices. Air tankers normally do not sit loaded with retardant in the Southeast. However, water is kept in the tanks, requiring that only the Pyro be added when a fire call is received. Thus, exposure of the aircraft and mixing system to retardant is minimized and retardant-caused corrosion should be minimal. This practice is not encountered in the West. A recent survey (August 2-7, 1974) of 47 western retardant bases having 73 aircraft available disclosed that 59 percent of the air tankers were required to sit loaded in readiness during the fire season, while only 5 percent of the air tankers never sit loaded. The remaining air tankers occasionally sit loaded (see data in DISCUSSION section). From this discussion, one might conclude that different performance requirements or specifications might be applicable for different parts of the country, depending on the type of fire problem, conditions of use, and the operational methods or practices.

In the Pacific Northwest Region, severe corrosion occurred on mixing, pumping, and storage facilities over an 8- to 10-year period, requiring extensive repair, refurbishing, and replacement of some equipment to maintain operational readiness. (Data on file at the Northern Forest Fire Laboratory, Missoula, Montana.) Retardant-caused corrosion occurring at these bases was primarily to mild steel although other alloys were often affected. The Pacific Northwest Region bases had used Fire-Trol 100 exclusively since the early 1960's. The ammonium sulfate based Fire-Trol 100 is adequately inhibited for aluminum (<1 mil/yr on Al-2024-T3) but exhibits significant corrosion to mild steel, brass, copper, and some other alloys.

Before making extensive repairs, Fire Management personnel from the Pacific Northwest Region decided to investigate the possibility of changing retardant types. Prior to the selection of a different fire retardant, fire control and equipment specialists traveled throughout the Southeast to look at the facilities and determine the needs for storing, mixing, and handling Pyro. The simplicity of the liquid system and apparent lower cost of manpower, hardware, and retardant were primary considerations which resulted in operational trials of a liquid retardant system in the Pacific Northwest Region at Lakeview, Oregon, and Wenatchee, Washington (Wood 1970). During 1969, 117,000 gallons of APP were dropped on 28 fires from aircraft operating out of these bases. In general, fire control personnel were favorably impressed with the effectiveness of APP in the Northwest. It was determined, however, that coloring in the formulation was necessary (it was first thought that a flag-type marking system would be adequate). When the costs of coloring, clay to hold the color in suspension, corrosion inhibitors, and transportation were included, the apparent cost advantages were substantially reduced. (The cost of Pyro in the South was considerably below costs for Pyro or other ammonium polyphosphate fertilizers (such as 10-34-0) encountered in the West. The cheaper cost for Pyro was primarily due to local marketing (Muscle Shoals, Alabama) by TVA (Tennessee Valley Authority), a Federal agency. In addition, the primary source of 10-34-0 in the Northwest was from Allied Chemical Company, which actually manufactures the product in Giesmar, Louisiana, and transports the material by ocean tankers to west coast outlets in Pasco, Washington, Portland, Oregon, and Wilmington and Richmond, California.)

It is important to note that direct effectiveness comparisons had been made with Fire-Trol 100 only. It is understandable that in experiences gained during operational use, the unthickened APP (Fire-Trol 931) was found to be equal or superior in effectiveness to the Fire-Trol 100 slurry. Considerable research (both laboratory and field tests) has been conducted to quantify the relative effectiveness of ammonium sulfate and ammonium phosphate compounds (George and Susott 1971; George and Blakely 1972; Johansen 1959). On an equal concentration basis, ammonium sulfate (as contained in Fire-Trol 100) is less effective in reducing the rate of spread and fire intensity than are ammonium phosphate compounds (George and Blakely 1972). This is because ammonium sulfate decomposes at a lower temperature (less than flame temperatures) than does ammonium phosphate and is thus not available to alter fuel pyrolysis and combustion reactions. In addition, drop tests (George and Blakely 1973; George 1975)

indicate little difference in the retardant breakup and drop characteristics between unthickened retardants (such as water and Fire-Trol 931) and the clay-thickened Fire-Trol 100. Although this phenomenon has been observed in numerous drop tests, only recently have we learned about the mechanisms involved.

Shock Hydrodynamics, under Forest Service contract (Andersen and others 1974b, 1974c), investigated the effects of retardant rheological properties, and determined that aerial breakup was not a function of apparent viscosity, as previously thought. Breakup characteristics were related to the effective viscosity, which incorporates the effect of shear rate and retardant elasticity. Under shear rates encountered during primary breakup ($10-1500\text{ s}^{-1}$), it was found that the gum-thickened retardants had a significantly higher effective viscosity than clay-thickened Fire-Trol 100, unthickened Fire-Trol 931, or water--which all had similar effective viscosities (table 1).

Although the Northern Forest Fire Laboratory had previously conducted a number of investigations (retardant evaluation quarterly reports on file at the Northern Forest Fire Laboratory, Missoula, Montana) to determine the effectiveness of liquid ammonium phosphate and polyphosphate solutions, the first evaluation of a complete formulation was in 1968 when Collier Carbon and Chemical Company (a subsidiary of Union Oil Company of California) submitted a thickened liquid ammonium phosphate product. The system involved the metered addition of calcium chloride into a diluted 8-24-0 liquid ammonium phosphate fertilizer. The calcium chloride reacted to form a tricalcium phosphate complex in suspension, creating a thickened slurry. Laboratory tests conducted at the Northern Forest Fire Laboratory and actual operational use from a base at Chino, California, indicated the sensitivity of the final slurry suspension to calcium chloride concentration, to the pH of the 8-24-0, and to shear during mixing, made it impossible to control rheological properties of the slurry.

Table 1.--Effective retardant viscosity during retardant breakup and application¹

Phase of drop	Shear rate	Effective viscosity (centipoise)				Water
		Phos-Chek	Fire-Trol	Fire-Trol	Fire-Trol	
		XA ²	100	931 (LC)		
Deformation	Low ($1-4\text{ s}^{-1}$)	3,700	10,000	500	1	
Liquid instability	Low to high ($10-1500\text{ s}^{-1}$)	1,400	200	50	1	
Surface erosion	Medium to high ($700-1400\text{ s}^{-1}$)	900	45	7	<1	
Fuel impaction ³	Low ($\sim 1-4\text{ s}^{-1}$)	$\sim 3,700$	$\sim 10,000$	~ 500	~ 1	

¹ Data from "Investigation of Retardant Rheological Properties," final report, Shock Hydrodynamics Division, Whittaker Corporation, North Hollywood, California, 1974.

² Phos-Chek XA contains a modified polysaccharide (guar gum) thickening agent and is representative of a "gum-thickened type" retardant.

³ Not yet completely quantified--approximately equal to values given for effective viscosities during the deformation phase.

In early 1968, Allied Chemical Company submitted Arcadian Poly-N 10-34-0 ammonium polyphosphate for evaluation. Several limiting factors were encountered--notably corrosion, lack of coloring and thickening agents, and storability. Allied, in cooperation with the Northern Forest Fire Laboratory, began testing several promising corrosion inhibitors. During this time, Arizona Agrochemical Corporation (now Chemonics Industries) began discussion with Allied and arrived at an agreement by which Chemonics Industries would cooperate in a developmental program using Allied Arcadian Poly-N for fire retardant use.² In August 1968, Chemonics Industries submitted Fire-Trol 931-A, the first of a series of formulations containing APP (Arcadian Poly-N), corrosion inhibitors, coloring agents, and attapulgite clay to suspend the coloring agent in the concentrate. Other Fire-Trol formulations followed (Fire-Trol 931-B, 931-C, and 931-D) with similar composition except for the corrosion inhibitor or inhibitors. Fire-Trol 931-D was the formulation used operationally on a trial basis in the Pacific Northwest Region the following year (1969). (The composition of each Fire-Trol 931 formulation is given in appendix A.)

Because Fire-Trol 931-A through 931-D did not initially meet the current Forest Service performance standards for either corrosion or solution stability (separation or storability), emphasis in the development and evaluation was placed on these properties. The retardant corrosion requirements became quite controversial for both fire control and research and development personnel. Requirements and specifications developed previously for thickened fire retardants (Phos-Chek XA and Fire-Trol 100) contained a corrosion performance requirement of ≤ 1 mil/yr on aluminum 2024-T3 and a tendency toward pitting of less than 5 (dimensionless numerical rating obtained with Magna Corrater model 1180) in addition to no evidence of intergranular corrosion.³

Pyro and APP advocates argued that the corrosion requirements were too stringent and the operational use of Pyro with little apparent corrosion was evidence that stated corrosion problems and 1 mil/yr requirements were unrealistic. Numerous corrosion problems, however, had been documented⁴ with mixing, handling, and storage equipment which was being used with retardants meeting the 1 mil/yr requirements (Fire-Trol 100 and Phos-Chek XA) (Davis and Phillips 1965). Because of this corrosion, R&D personnel took the position that since ≤ 1 mil/yr corrosion rate on Al-2024-T3 had been achieved with Phos-Chek XA and Fire-Trol 100, the same performance should be required for the APP formulations if that level of performance was practically and economically attainable. (The 1 mil/yr requirement on Al-2024-T3 can be attained since an APP formulation (10-34-0, coloring, and corrosion inhibitors) submitted by Stauffer Chemical Company has been evaluated and met the requirement. Although it appeared that the formulation would be approved, Stauffer withdrew it from evaluation prior to final approval.)

To resolve the controversy over corrosion requirements, a contract was let by the Forest Service to Ocean City Research Corporation (OCRC) in June 1973. Ocean City Research Corporation, which specializes in corrosion research and consultation, conducted field surveys of aircraft and retardant plant facilities, performed laboratory corrosion tests on present retardant formulations and on alloys determined critical during the field survey, and investigated new inhibitors and protective systems (Gehring 1974). The program was designed to quantify the extent of actual corrosion occurring in the field, correlate the results with laboratory results, and make recommendations for performance requirements, evaluation methods, procedures for minimizing damage, and alloys to avoid using. The initial program has been completed and a summary of conclusions and

²Private communication with Allied Chemical Company and Chemonics Industries personnel.

³USDA Forest Service Interim Specifications, 1969-1970.

⁴Retardant evaluation quarterly status reports on file at the San Dimas Equipment Development Center, San Dimas, California.

recommendations is given in Appendix B. Additional research about the problem is being conducted by both the Forest Service and OCRC under a contract amendment.⁵

During this period, Chemonics Industries submitted numerous liquid phosphate formulations containing different corrosion inhibitors and types (manufacturers or manufacturing process) of ammonium polyphosphate in an attempt to achieve a corrosion rate of <1 mil/yr on Al-2024-T3 as determined by the Magna Corrater and as outlined in USDA Forest Service Specifications 5100-00301 and 5100-00302a. (Retardants for ground application (type G) also required a corrosion rate of <3 mil/yr on Al-2024-T3, mild steel AISI C-1010, prime western (ASTM) zinc, and free-cutting brass (Fed. Spec. QQ-B-626 composition 22).)

Fire-Trol 931-D was first used operationally in the Pacific Northwest Region under interim approval by Washington Office Fire Management and purchased under Forest Service Specification 5100-00302a. Exceptions allowed a uniform corrosion rate of 5 mil/yr (0.005 in) on Al-2024-T3 and a separation of 12 percent by volume (specification requirements were 1 mil/yr and 5 percent separation by volume).

The formulation (Fire-Trol 931-D) contained sodium dichromate corrosion inhibitor and Allied Poly-N 10-34-0 APP. In the summer of 1972, the manager of The Dalles, Oregon, city water treatment and watershed became concerned about the Pacific Northwest Region's use of retardant containing "toxic elements as a part of their chemistry," referring to hexavalent chromium. (Correspondence on file at the Northern Forest Fire Laboratory, Missoula, Montana.) After much deliberation, the Fire-Trol 931-APP formulation was altered; the sodium dichromate was replaced by a corrosion inhibitor system composed of sodium thiosulfate, sodium molybdate, and sodium 2-mercaptobenzothiazole (Fire-Trol 931-J). The manufacturer encountered problems with the latter ingredient while blending the concentrate (the dust caused irritation to personnel when the dry material was being added to the liquid concentrate). Therefore, the mercaptobenzothiazole was dropped from the formulation.⁶ The resultant formulation (Allied Poly-N 10-34-0, sodium thiosulfate and sodium molybdate corrosion inhibitors, attapulgite clay, and iron oxide coloring) has never been submitted to and tested by the Forest Service. The inhibitor system, however, satisfied the environmental and health hazard concerns of The Dalles personnel and others but likely exceeds the corrosion rate requirement of less than 1 mil/yr on Al-2024-T3 (previous corrosion tests on Fire-Trol 931-J indicated a corrosion rate of approximately 5 mils/yr).

In November 1973, Chemonics Industries submitted a Fire-Trol 931-L (APP) containing sodium ferrocyanide (YP soda)⁷ as a corrosion inhibitor for the Allied Poly-N 10-34-0 formulation. The new inhibitor reduced the corrosion rate as tested in accordance with specifications to <1 mil/yr. This formulation has been tested by the Northern Forest Fire Laboratory and San Dimas Equipment Development Center and is one of the primary formulations whose performance is outlined later in this report. This formulation, however, was not being used operationally from air tankers. The Boise National Forest (air tanker base at Boise, Idaho), rather than using Allied Poly-N 10-34-0, was using a

⁵"Laboratory investigation of fire retardant-caused corrosion," study plan 2107-500, on file at the Northern Forest Fire Laboratory, Missoula, Montana, and Forest Service contract 26-3250 to Ocean City Research Corporation, Ocean City, New Jersey.

⁶Private communication with Kathy Lacey, Chemist, Chemonics Industries, October 1974.

⁷Chemonics Industries has a patent pending for use of sodium ferrocyanide inhibitor in ammonium polyphosphate base forest fire retardants.

Simplot-produced superphosphoric acid which was being ammoniated by local fertilizer dealers under verbal agreement to Chemonics Industries (Feed Service, Caldwell, Idaho, was formulating Fire-Trol 931-P utilized at the Boise Air Tanker Base).⁸

Because fire and fuel characteristics and retardant drop conditions often vary and have different requirements, a system which would allow independent selection of the salt content and rheological properties (especially effective viscosity) potentially provides the fire control specialist with the capability to tailor the retardant properties to the specific fire situations. This concept was discussed in an article "Liquids fight forest fires" published in *Fertilizer Solutions* magazine (November-December 1971) with a headline: "Searching for new fire retardant system, the Forest Service challenges the liquid fertilizer industry to produce a better product..." (George 1971b).

Chemonics Industries decided to meet this challenge and began the research and development for a new thickened APP retardant system. This decision was stimulated by the Bureau of Land Management (BLM) fire control personnel at Boise, Idaho, who recognized the need for improving the drop characteristics of the unthickened APP being used, and requested such a product. These personnel had experienced excessive dispersion and drift, resulting in reduced effectiveness under some conditions and fire situations. The thickened APP formulations previously evaluated were considered first (invert-emulsion-thickened 10-34-0 systems produced by both Petrolite Corporation and Stull Chemical Company had previously been evaluated in the laboratory and during drop tests at Porterville, California). In drop tests, the invert-emulsion-thickened retardants showed poorer drop characteristics than the gum-thickened retardants, although all were superior to the unthickened APP solutions. (1972 Marana drop tests. Data on file at the Northern Forest Fire Laboratory, Missoula, Montana.) Test drops of Petrolite-thickened Fire-Trol APP solutions on actual fuels indicate that damage to vegetation (including mature trees) may result--probably caused by the Petrolite thickening agent (inverter). Chemonics Industries has terminated tests until the cause for the apparent toxicity has been determined.

In November 1973, Chemonics Industries submitted two thickened APP retardant formulations: gum-thickened Fire-Trol 931-L and Petrolite invert-emulsion-thickened Fire-Trol 931-L. After preliminary laboratory tests were completed, cooperative agreements were entered between Chemonics Industries and the Intermountain Forest and Range Experiment Station, Northern Forest Fire Laboratory; planning for immediate drop testing began.⁹

Drop tests with the new thickened APP products were conducted at Marana, Arizona, during January and February 1974. Analysis of test results indicated that gum-thickened Fire-Trol 931-L was superior to the invert-emulsion-thickened Fire-Trol 931-L, and that a 2,000 cP apparent viscosity for the gum-thickened solutions gave approximately the same drop performance as the previously quantified gum-thickened Phos-Chek XA fire retardant. (The drop performance of the gum-thickened Fire-Trol 931-L is shown in Section 3.1.15., Air Drop Characteristics.)

The BLM and Boise National Forest decided to evaluate the gum-thickened Fire-Trol 931-L operationally during the 1974 fire season at Boise. Fire-Trol 931-L was not being used, but it was expected that drop characteristics would be similar to those of the product being used (Fire-Trol 931-P; and thus gum-thickened Fire-Trol 931-P). The major problem at this point was the development of a proportioning system for the gum thickener

⁸Private communications with representatives of the companies mentioned. Fire-Trol 931-P is presently being evaluated by the Northern Forest Fire Laboratory and the San Dimas Equipment Development Center.

⁹Cooperative agreements are outlined in INT Study Plan 2107-17G, on file at the Northern Forest Fire Laboratory, Missoula, Montana.

which would provide adequate quality control at preselected levels of gum and APP concentration. Chemonics and Developmental Sciences Incorporated developed such a system and installed it at the Boise base. Although the equipment was used operationally, there were problems in maintaining accurate, reliable control of the chemical and physical retardant properties at preselected levels. When the retardant quality was known, fire control personnel were able to perform adequate on-the-fire evaluations. They concluded that gum-thickened retardants definitely improved retardant drop characteristics and on-site fire retarding effectiveness.¹⁰ (During operational evaluation, a goal was to achieve effectiveness from higher and safer average drop heights between 150 and 300 feet.)

EVALUATION OF FIRE-TROL 931 APP FORMULATIONS

The performance of the Fire-Trol 931-APP formulations that have been evaluated is given in this section. The evaluation was performed as specified in Forest Service Specification 5100-00302a unless otherwise noted. (The paragraph numbers refer to qualification requirements as outlined in the specification.)

Storage (3.1.1.)

Requirements: The liquid concentrate shall be stored in two 10-gallon sealed, mild steel containers for a period of 1 year. One container shall be subjected to outside environmental conditions at Missoula, Montana, and the other container subjected to outside environmental conditions at San Dimas, California (fig. 1). After 1-year storage, the liquid concentrate must meet all requirements defined in the specification, and the "mixed retardant" (liquid concentrate mixed with water according to retardant proportions specified by the manufacturer) shall meet the requirements related to viscosity (3.1.3.), separation (3.1.12.), and spoilage (3.1.13.). The mixed retardant shall not exhibit more than 5 percent by volume separation for a period of 4 hours after mixing (temperature at 75 $\pm 5^\circ$ F).

Performance: Fire-Trol 931-L, 931-N, 931-P, and thickening agents are currently being stored at Missoula and San Dimas. Storage tests were initiated shortly after the dates submitted samples were received, as follows:

	Sample	Date received	Date storage tests initiated
APP concentrates	-Fire-Trol 931-L	1/2/74	8/1/74
	-Fire-Trol 931-N	5/5/74	8/1/74
	-Fire-Trol 931-P	7/26/74	8/1/74
Thickening agents	-Liquid gum thickener	7/29/74	8/1/74
	-Petrolite invert emulsifier	3/3/74	8/1/74

¹⁰Personal communication with Bureau of Land Management Fire Management personnel.

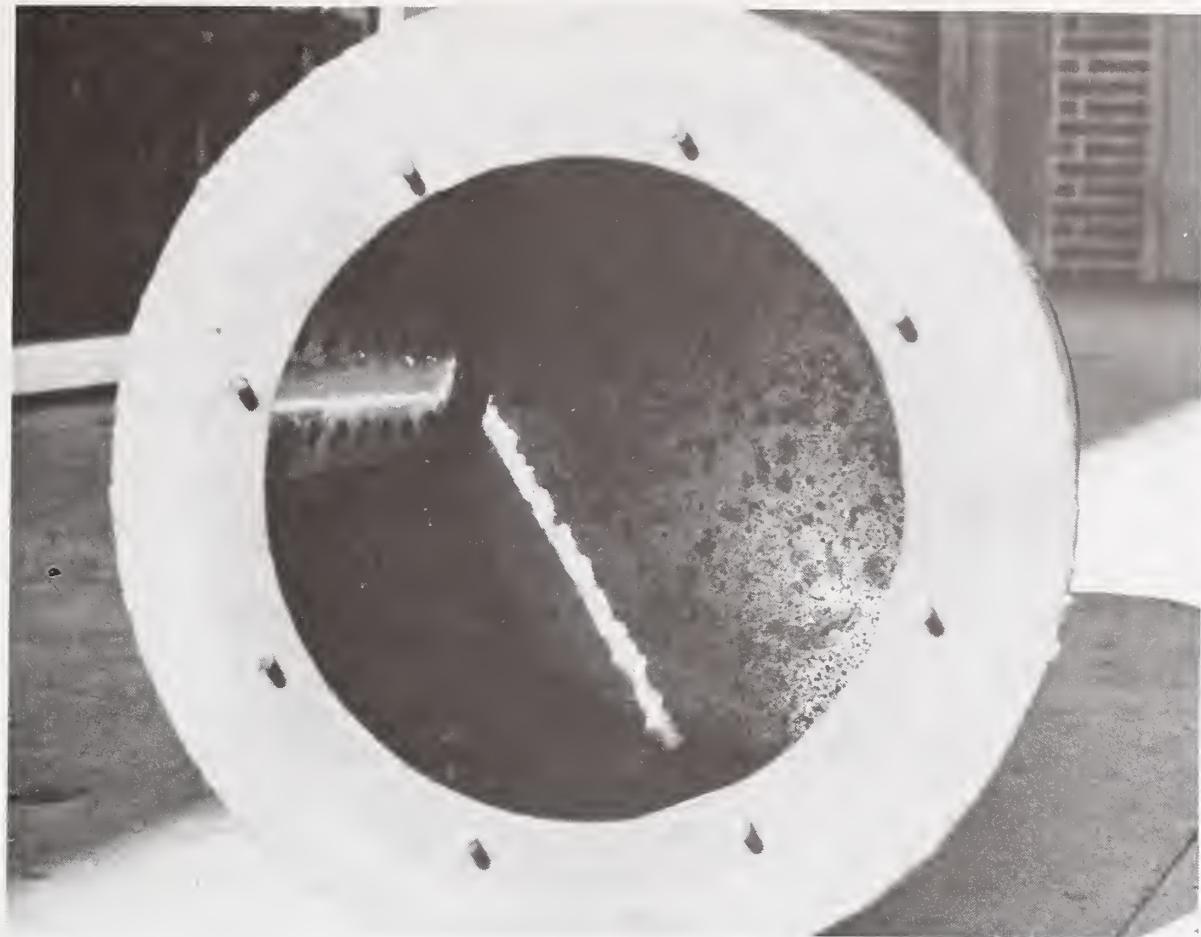


Figure 1.--Mild steel storage container (10 gallon) with plexiglass slot for visually inspecting the retardant during the long-term storage tests (above). Outdoor storage rack containing 10-gallon retardant storage samples (below).

Liquid concentrate storage (4.3.1.1.): The performance of the liquid concentrate and the mixed retardant (prepared from the stored concentrate) has been determined during the prescribed storage period. Visual inspection revealed slight separation in the APP concentrate samples. Color gradations are present and may indicate a separation of colloidal particles by size class. A typical blue color (due to presence of the sodium ferrocyanide corrosion inhibitor) is evident where the liquid and the mild steel are in contact as well as on the surface of the liquid.

The Petrolite invert emulsifier showed complete solution stability. The liquid gum thickener, however, had significant separation--the gum settled from the upper 20 percent of the liquid carrier. The gum thickener alone does not meet the storage requirements.

Mixed retardant storage (4.3.1.2.): The mixed retardant was stored in 1-quart glass jars, half of them containing a mild steel coupon (1 by 1 by 1/8-inch in size). This test was conducted on a sample prepared from the stored concentrate; however, separation performance was not expected to be significantly different. The separation rate for all mixed retardant samples tested indicates that the solution is not stable (>5 percent separation) for 4 hours after mixing (discussed further under Separation, 3.1.12.). The mixed retardant therefore does not meet the requirements for storage.

Specific Weight (3.1.2.)

Requirements: The liquid concentrate and the mixed retardant will be tested for specific weight at room temperature ($70 \pm 5^\circ$ F). A test sample of the retardant solution will be allowed to sit for at least 1 hour to allow egress of any entrained air. The specific weight will be determined using a pycnometer or by accurately weighing a gallon of the solution. The specific weight of the mixed retardant shall not exceed 9.5 pounds/gallon.

Performance: The specific weight of the concentrates, mixed retardants, thickening agents, and thickened retardant solutions is:

Retardant	Specific weight	
	Concentrate (lb/gal)	Mixed retardant @ 4:1 dilution rate (lb/gal)
Fire-Trol 931-L	12.32	9.19
Fire-Trol 931-N	12.16	9.21
Fire-Trol 931-P	12.23	9.22
Liquid gum thickener	10.00	
Petrolite inverter	6.93	
Gum-thickened		
Fire-Trol 931-L (1.5 percent gum)		9.21
Petrolite-thickened		
Fire-Trol 931-L (4 percent Petrolite inverter)		9.20

Because the Fire-Trol 931-APP solutions can be used effectively at concentrations (dilution rates) other than the standard 4:1 concentration, it is often necessary to relate specific weights to dilution rates and salt concentrations (P_2O_5 equivalent). A standard procedure for determining the salt content in the field (George 1971a) is to use calibration tables that correlate specific gravity of a prepared filtrate solution to salt content and dilution rate. Such tables for calibration and

field determination of salt content and thus retardant quality have been determined for Fire-Trol 931-L, 931-N, and 931-P. Although calibration tables are slightly different for the three formulations, the differences are probably not significant for quality control purposes in the field. Table 2 provides the data for Fire-Trol 931-P (which represents approximate mean values for the three products). The lined area indicates a satisfactory salt content exists and no adjustment is needed. The satisfactory salt content was determined by allowing approximately a 10 percent

Table 2--Fire-Trol 931-P salt content as related to specific gravity¹

Dilution rate ²	Measured specific gravity of filtrate	Percent P ₂ O ₅ equivalent (by weight)	Percent DAP (NH ₄) ₂ HPO ₄ (by weight)
10:1	1.043	4.1	7.6
9:1	1.047	4.4	8.2
8:1	1.053	4.9	9.1
7:1	1.060	5.5	10.2
	1.065	5.9	11.0
6:1	1.069	6.2	11.6
	1.070	6.3	11.8
	1.073	6.6	12.2
	1.075	6.7	12.5
5:1	1.080	7.2	13.3
	1.085	7.5	14.1
	1.090	8.0	14.9
	1.095	8.4	15.6
4:1	1.096	8.5	15.8
	1.100	8.8	16.4
	1.105	9.2	17.2
	1.110	9.6	17.9
	1.115	10.1	18.7
3:1	1.119	10.4	19.3
	1.120	10.5	19.5
	1.125	10.9	20.3
	1.130	11.3	21.0
	1.135	11.7	21.8
	1.140	12.1	22.6
	1.145	12.5	23.3
	1.150	13.0	24.1
2:1	1.155	13.4	24.9
- - - - -			
Expanded scale			
	1.175	15.0	28.0
	1.200	17.1	31.8
1:1	1.221	18.8	35.1
	1.225	19.2	35.7
	1.250	21.3	39.5

¹ The recommended use level for Fire-Trol 931-P is four parts water to one part concentrate (by volume). An adequate specific gravity and salt content corresponding to this use level is outlined within the table. Values for salt content were determined from the equation: Percent P₂O₅ equivalent = 83.02 specific gravity - 82.51.

² Ratio of volume of water added to volume of concentrate.

deviation above and below the recommended salt content. (Values in this table are slightly different from those previously published (George 1971a), due to differences in the basic types of 10-34-0 APP and the formulation (corrosion inhibitors, coloring agents, and other additives).) All of the retardants tested meet the requirement for specific weight.

Viscosity (3.1.3.)

Requirements: The viscosity of the liquid concentrate and the mixed retardant will be determined before and after the storage period outlined under Storage (3.1.1.). The viscosity of thickened APP samples as mixed for use will be determined at appropriate time intervals depending on the stability of thickened slurry; thus, defining a viscosity versus time following mixing curve. The viscosities will be determined using a Brookfield Viscometer, Model LVT or LVF, at 60 r/min with the appropriate spindle. (Spindle No. 2 for viscosities 1-500 cP, spindle No. 4 for viscosities greater than 500 cP.) An average viscosity will be determined from three readings on 1,000 ml retardant samples held at a temperature of $70 \pm 5^{\circ}$ F. The viscosity of the mixed retardant shall not exceed 200 centipoise and the viscosity of gum-thickened APP solutions shall be 1,000-2,000 cP. (No specification exists for a thickened liquid retardant. It is assumed performance requirements shall be the same as those for a thickened, dry chemical retardant (Forest Service Specification 5100-00301). This assumption is made because on-site retardant requirements should be the same for a solution regardless of whether it was prepared from a liquid or dry ammonium phosphate salt.)

Performance: The average viscosities of the Fire-Trol 931 APP concentrate and "mixed retardant" are given below:

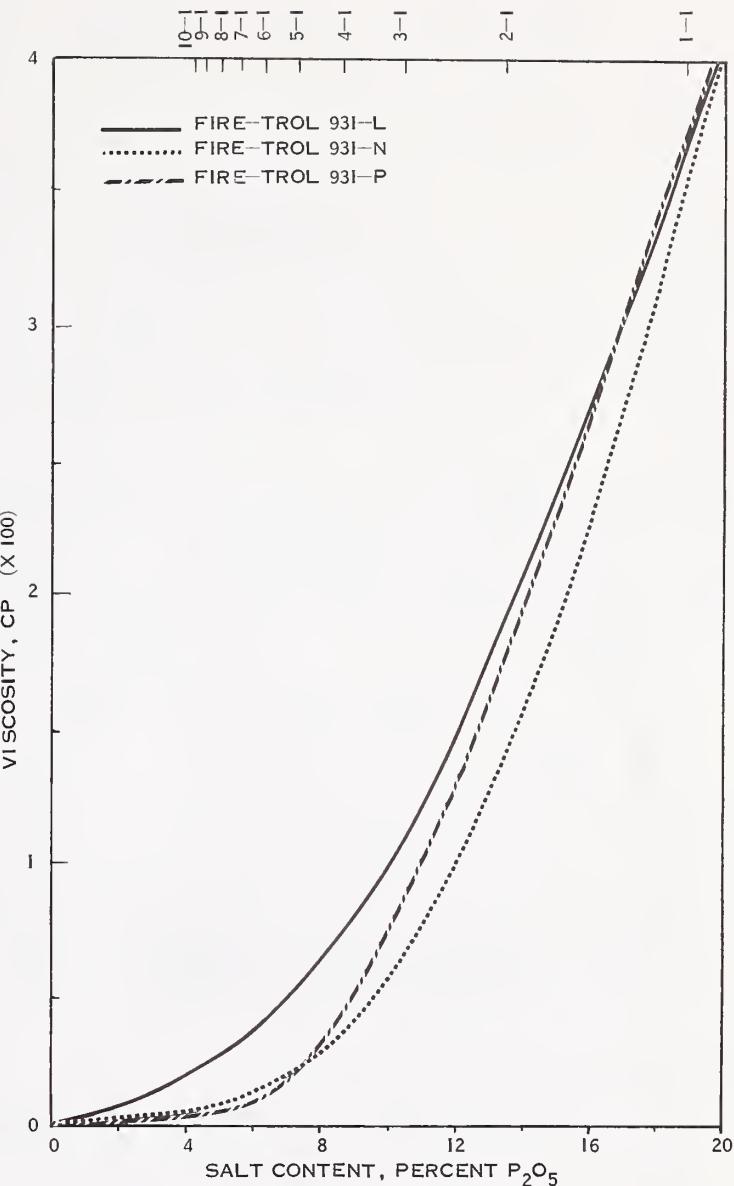
Retardant	Brookfield viscosity (cP)
Fire-Trol 931-L (concentrate)	4,336
Fire Trol 931-L (mixed 4:1)	81
Fire-Trol 931-N (concentrate)	3,661
Fire-Trol 931-N (mixed 4:1)	22
Fire-Trol 931-P (concentrate)	2,263
Fire-Trol 931-P (mixed 4:1)	34
Gum thickener (concentrate)	4,557 (sample #1) 2,326 (sample #2)
Petrolite invert emulsifier (concentrate)	32

The viscosities of the concentrate Fire-Trol 931 APP solutions vary considerably, as shown by the data above. The viscosity of these solutions is a function of the amount of shear or mixing given the solution during its preparation. As noted by their composition (appendix A), these solutions contain attapulgite clay, which derives its viscosity by separation of lattice layers and inclusion of water between these layers. The degree of separation of these layers is determined by the amount of shear given the clay. A viscosity of at least 1,500 cP is required for the resulting slurry to maintain a stable colloidal suspension.

The viscosity of the diluted mixed solution (unthickened) is a function of the dilution rate or salt concentration and the initial viscosity of the concentrate. Figure 2 shows a plot of the viscosities of Fire-Trol 931-L, 931-N, and 931-P as a function of dilution rate. Although differences in viscosity can be seen, it is very doubtful that these viscosity changes significantly affect mixing, pumping, drop characteristics, and distribution within the fuel complex.

The viscosity of the gum-thickened Fire-Trol 931 APP solutions is a function of the dilution rate of the retardant, the amount or concentration of the gum thickener

Figure 2.--Viscosity of unthickened Fire-Trol 931-L, 931-N, and 931-P as a function of retardant salt content.



used, and the hydration time following mixing (the hydration rate is also a function of the mixing history--shear rate, time, etc.). Figures 3, 4, and 5 indicate the effect of gum concentration and hydration time on the viscosity development of three different dilutions of Fire-Trol 931-L (2:1, 4:1, 6:1). Similar curves are being developed for Fire-Trol 931-N and Fire-Trol 931-P. Although slight differences in viscosity are expected for the latter two products (due to differences in the basic 10-34-0 solutions), the quality of the gum concentrate will likely be more important. Storage tests to date indicate the quality of the gum concentrate affects the resulting viscosity and the stability of the solution to a greater degree than does the type of 10-34-0. This effect is shown by comparing viscosities (measured after 1 hour and the maximum viscosity developed) for samples of Fire-Trol 931-L diluted 4:1 containing 1.5 percent of gum thickener which had been stored for various lengths of time:

Length of gum storage (Weeks)	Viscosity at 1 hour (cP)	Maximum viscosity developed (cP)
- - - - - Fire-Trol 931-L 4:1 + 1.5 percent gum thickener - - - - -		
0	1,200	1,670
4	900	>900
7	957	1,143
9	1,013	1,240
18	990	1,110

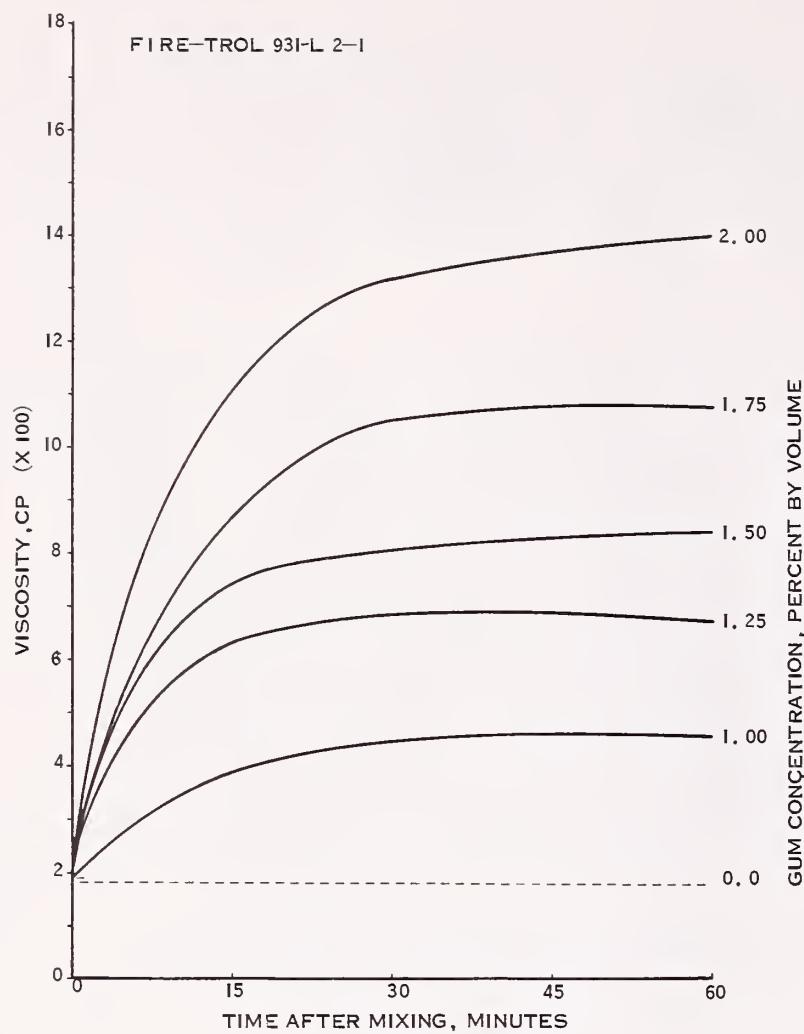


Figure 3.--The effect of time following mixing (hydration time) on the viscosity of a Fire-Trol 931-L solution (2:1 dilution) for several concentrations of gum thickener.

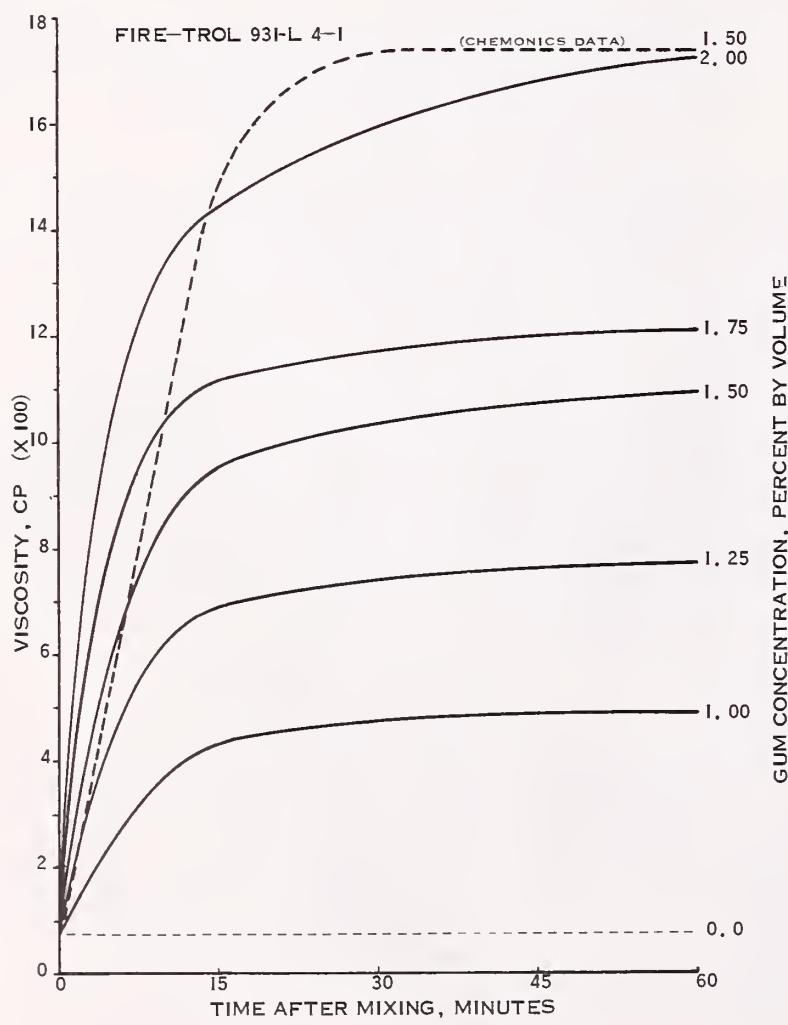


Figure 4.--The effect of time following mixing (hydration time) on the viscosity of a Fire-Trol 931-L solution (4:1 dilution) for several concentrations of gum thickener.

Figure 5.--The effect of time following mixing (hydration time) on the viscosity of a Fire-Trol 931-L solution (6:1 dilution) for several concentrations of gum thickener.

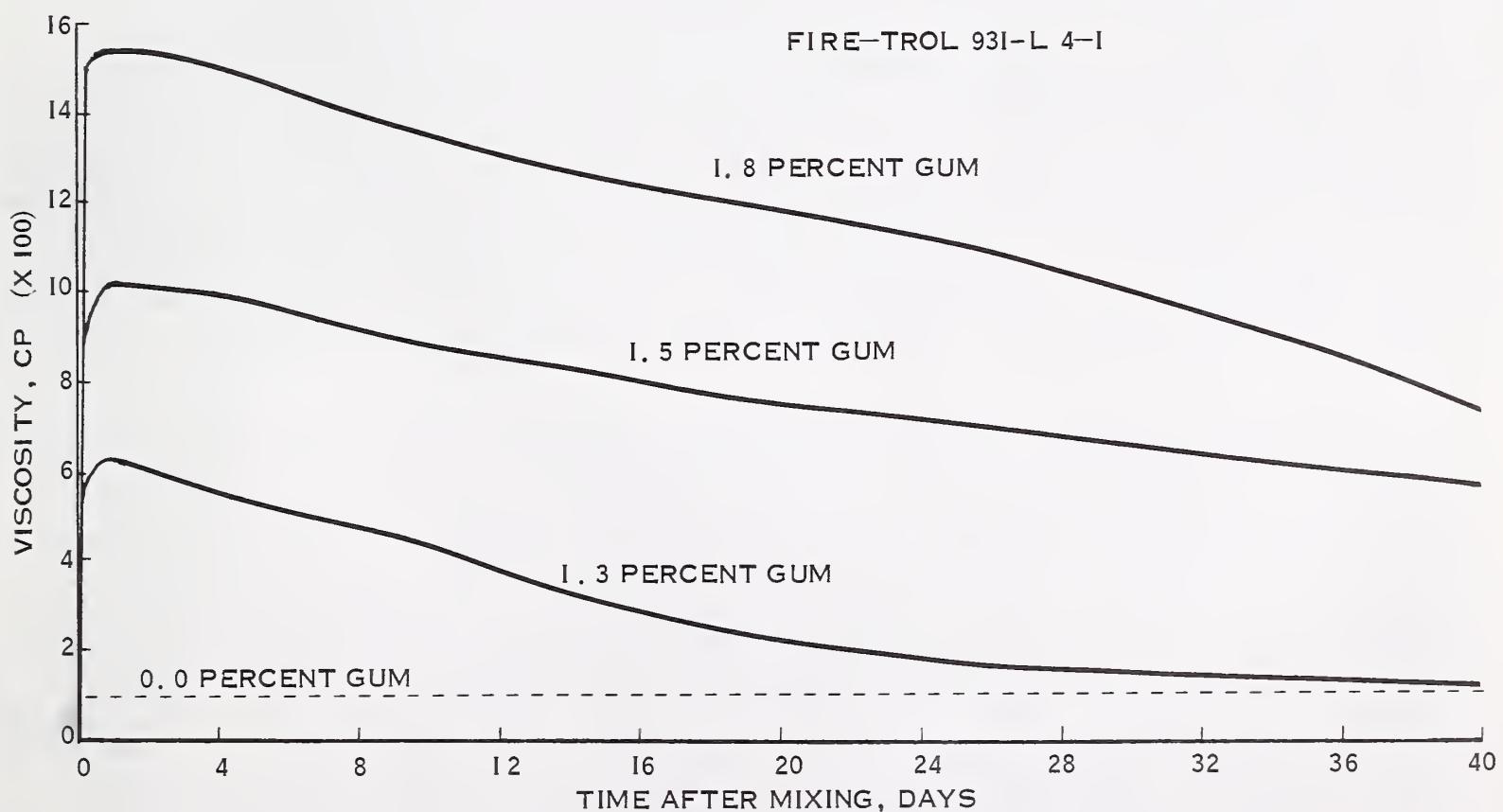
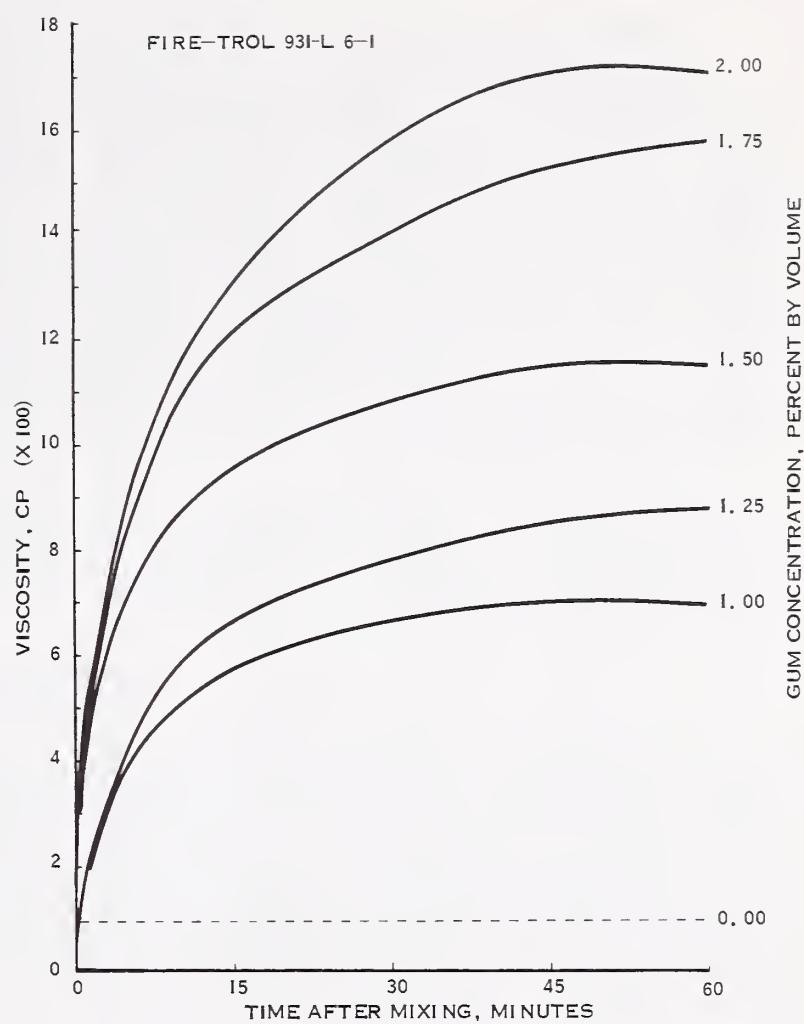


Figure 6.--The effect of storage time (time after mixing) on the viscosity of 4:1 dilution of Fire-Trol 931-L containing gum thickener at several concentrations.

As previously noted, the storage requirement for an unthickened mixed retardant is a 4-hour stability period (separation <5 percent at the end of 4 hours), while for a thickened mixed retardant the solution must maintain stability for 1 year. Because of the demand mixing capability with the thickened liquid system and the frequent practice of having air tankers stand by loaded, an intermediate storage requirement might be warranted (such as 2 weeks to 1 month solution stability). In view of the differing requirements for the dry-type thickened retardant and the unthickened liquid retardant, storage stability was quantified over a period of time covering both requirements. The viscosity of Fire-Trol 931-L mixed at a dilution of 4:1, with various concentrations of gum thickener and shown as a function of time since mixing, is given in figure 6. The 1.5 and 1.8 percent gum mixtures thicken to over 1,000 cP within the first hour; they drop below that level in 4 and 30 days, respectively.

Unthickened Fire-Trol 931-L, 931-N, and 931-P meet the viscosity requirement of less than 200 cP. When thickened, Fire-Trol 931-L does not fulfill the requirement for thickened retardants (dry retardant specification) because of the decrease in viscosity during the first 4 days.

Corrosion (3.1.4.)

Requirements (uniform corrosion and pitting tendency 3.1.4.1. and 3.1.4.2.): The liquid concentrate and mixed retardant for aerial application (type A) and ground application (type G) will be tested for uniform corrosion and pitting tendency using a corrosion rate meter (Magna corrater, or equal). The alloy to be tested will be used as the electrode probes in determining the uniform corrosion rate and the pitting tendency. Aluminum alloy 2024-T3 will be used for both type A and type G retardants. In addition to Al-2024-T3, type G retardants will be tested using probes of mild steel AISI C-1010 and naval brass.

The appropriate metal probe will be immersed in the retardant test sample under static conditions for 16 hours. The conditioned probe will then be immersed into the sample under dynamic conditions (sample rotating at 1 r/min) for 8 hours, and then gently rinsed with lukewarm water. After the probes have dried, they will be reimmersed in the sample and monitored for an additional 8 hours, after which they will be rinsed with a high pressure stream of water to simulate actual aircraft washdown. The probes will be dried again, and then immersed under dynamic conditions for an additional 8 hours. The uniform corrosion rate will then be determined. The uniform corrosion rates for type A concentrate or mixed retardants shall be ≤ 1 mil/yr (0.001 in/yr) and for type G concentrate or mixed retardants shall be ≤ 3 mils/yr (0.003 in/yr). The pitting tendency for both type A and G retardants shall not exceed a factor of 5.0.

Performance (uniform corrosion and pitting tendency 3.1.4.1. and 3.1.4.2.): The average uniform corrosion rate and pitting tendency for several Fire-Trol 931 APP concentrates and mixed retardants on aluminum 2024-T3 are given in table 3. This table includes several dilution rates other than the standard 4:1 dilution, since the manufacturer suggests possible use of various dilution rates in addition to the 4:1 dilution rate. Figure 7 shows that as the concentration of Fire-Trol 931-L is increased from 25:1 to 10:1 the uniform corrosion rate on Al-2024-T3 increases. With additional increases in concentration beyond 10:1, the uniform corrosion rate decreases. To determine this relationship for each retardant formulation would require a very large number of tests and considerable time; therefore, only comparative data at selected dilution rates have been determined for Fire-Trol 931-N and 931-P (table 4). At all concentrations tested, Fire-Trol 931-N is either under or just slightly over 1 mil/yr and all Fire-Trol 931-P concentrations tested are under 1 mil/yr.

Table 3.--Uniform corrosion rates and pitting tendency on Al-2024-T3 alloy for Fire-Trol APP retardant solutions tested

Retardant	Concentrate			Diluted for use			
	Number of runs	Uniform corrosion rate	Pitting tendency	Dilution rate	Number of runs	Uniform corrosion rate	Pitting tendency
		(mils/yr)				(mils/yr)	
Fire-Trol 931	2	0.5	0.07	4-1	3	5.5	5.4
Fire-Trol 934	1	.42	1.4	4-1	1	4.9	2.5
Fire-Trol 931-A	1	7.9	.8	4-1	1	14.0	4.0
Fire-Trol 931-B	2	.24	.55	4-1	2	2.6	1.4
Fire-Trol 931-C	2	.09	.16	4-1	2	2.9	1.2
Fire-Trol 931-D	2	.74	.31	4-1	2	2.1	.4
Fire-Trol 931 Dryden, Canada	1	.75	1.07	4-1	1	3.4	.5
Fire-Trol 931-E	9	.3	.15	4-1	6	1.1	.1
Fire-Trol 931-F	9	.45	.19	4-1	6	2.5	.2
Fire-Trol 931-J	6	2.0	.8	4-1	6	4.4	.9
Fire-Trol 931-L	3	.23	.15	4-1	18	.79	1.78
do.				7-1	6	.93	1.99
do.				6-1	9	.73	2.59
do.				5-1	6	.48	1.31
do.				3-1	3	.13	.63
do.				2-1	3	<.1	.47
do.				10-1	3	1.13	1.7
do.				25-1	6	.73	4.35
Fire-Trol 931-N	3	.07	3.23	4-1	16	.85	2.87
do.				7-1	6	1.01	1.20
do.				6-1	6	.55	.66
do.				5-1	9	1.01	1.44
do.				3-1	6	1.27	2.42
Fire-Trol 931-P	6	.37	.47	4-1	12	.48	1.70
do.				7-1	6	.35	.93
do.				6-1	9	.88	.79
do.				5-1	6	.69	1.17
do.				3-1	6	.62	1.10



Figure 7.--Uniform corrosion rate of Al-2024-T3 as a function of salt content for Fire-Trol 931-L.

Table 4.--Uniform corrosion rates and pitting tendency on A1-2024-T3 alloy for unthickened Fire-Trol 931-N and 931-P.

Dilution rate	Analyzed salt content	Number of runs	Uniform corrosion	Pitting tendency
Percent P_2O_5				Mils/yr
FIRE-TROL 931-N				
H_2O	0.0	3	0.104	0.06
7:1	5.66	6	1.01	1.20
6:1	6.43	6	.55	.66
5:1	7.23	9	1.01	1.44
4:1	8.66	16	.85	2.87
3:1	10.77	6	1.27	2.42
Conc.	32.67	3	.07	3.23
FIRE-TROL 931-P				
H_2O	0.0	3	.104	.06
7:1	5.71	6	.35	.93
6:1	6.69	9	.88	.79
5:1	7.64	6	.69	1.17
4:1	8.84	12	.48	1.70
3:1	10.41	6	.62	1.10
Conc.	32.41	6	.37	.47

Similar corrosion tests were run on gum-thickened Fire-Trol 931-L, as well as the concentrated liquid gum-thickening agent and the Petrolite inverter. The results of these corrosion tests are given in table 5. Corrosion rates for gum-thickened Fire-Trol 931-N and 931-P, mixed 4:1, are also given. One 2:1 dilution and a 6:1 dilution of Fire-Trol 931-L have uniform corrosion rates above 1 mil/yr. All other mixtures with various dilution rates and amounts of gum thickener have corrosion rates less than 1 mil/yr.

Although Fire-Trol 931 is considered a type A retardant (for aerial application) and not normally for use as a type G retardant (for ground application), several tests were run on the alloys specified for type G retardants (mild steel, brass, and zinc [3.1.4.2.]). Corrosion rates for these alloys when exposed to several Fire-Trol 931 formulations are given in table 6. On brass and 1010 steel, only Fire-Trol 931-N concentrate has a corrosion rate higher than 1 mil/yr. All materials tested on zinc show high corrosion rates of over 450 mils/yr.

The investigation of retardant-caused corrosion performed by Ocean City Research Corporation (Gehring 1974) has better defined the effects of these formulations on several types of corrosion; i.e., uniform or general, galvanic, crevice, fatigue, stress, etc. Although current retardant specifications do not contain requirements for corrosion other than those outlined in this section for uniform corrosion and pitting tendency (3.1.4.2.) and intergranular corrosion (3.1.4.3.), the corrosion characteristics of

Table 5.--Uniform corrosion rates and pitting tendency on Al-2024-T3 alloy for gum-thickened Fire-Trol 931-L, 931-N, and 931-P

Retardant	Dilution rate	Amount of gum	No. of runs	Uniform corrosion (Mils/yr)	Pitting tendency
(Percent by weight)					
Petrolite inverter	Conc.		3	0.20	0.83 ¹
Gum thickener (old drum)	Conc.		3	<.01	.1
Gum thickener (new drum)	Conc.		3	<.01	.03
Fire-Trol 931-L	2:1	1.3	3	1.58	1.73
do.	2:1	1.5	3	.51	.63
do.	2:1	1.8	3	.29	.55
do.	3:1	1.3	3	.32	.22
do.	3:1	1.5	3	.19	.44
do.	3:1	1.8	3	.18	1.32
do.	4:1	1.3	3	<.01	1.30
do.	4:1	1.5	3	<.01	2.00
do.	4:1	1.8	5	.24	.60
do.	5:1	1.3	3	.05	.58
do.	5:1	1.5	3	.21	.24
do.	5:1	1.8	2	.21	.075
do.	6:1	1.3	3	<.01	3.33
do.	6:1	1.5	3	.17	1.67
do.	6:1	1.8	3	1.12	.74
Fire-Trol 931-N	4:1	1.3	3	.25	.51
Fire-Trol 931-P	4:1	1.3	3	.81	1.08

¹ Visual inspection of Corrater probes following these tests indicates significant pitting although the instrument data indicated a pitting tendency of 0.83.

Table 6.--Uniform corrosion rates and pitting tendency on zinc, brass, and (1010) steel for Fire-Trol 931 formulations tested

Retardant	Dilution rate	Number of runs	Uniform corrosion Mils/yr	Pitting tendency
ZINC				
Fire-Trol 931-D	4:1	3	456	90
Fire-Trol 931-L	Conc.	3	921	0
Fire-Trol 931-L	4:1	3	initial rate >1000 mil/yr	
BRASS				
Fire-Trol 931-D	4:1	3	0.94	0.9
Fire-Trol 931-L	Conc.	3	.15	.03
Fire-Trol 931-L	4:1	3	.43	.1
Fire-Trol 931-N	Conc.	3	.897	.09
Fire-Trol 931-N	4:1	3	.637	.17
Fire-Trol 931-P	Conc.	3	.056	.05
Fire-Trol 931-P	4:1	3	.148	.06
1010 STEEL				
Fire-Trol 931-D	4:1	3	.86	.30
Fire-Trol 931-L	Conc.	3	.17	.18
Fire-Trol 931-L	4:1	3	.56	.87
Fire-Trol 931-N	Conc.	3	1.88	1.56
Fire-Trol 931-N	4:1	3	.581	.062
Fire-Trol 931-P	Conc.	3	.418	.43
Fire-Trol 931-P	4:1	3	.916	.04

these products and alloys are of considerable interest to retardant users. Therefore, test results and subsequent recommendations are summarized in the discussions and in appendix B.

Requirements (Intergranular Corrosion 3.1.4.3.): Intergranular corrosion will be measured for type A liquid concentrates and the mixed retardant, using U-bend 2024-T3 aluminum test samples. Two individual U-bend samples will be exposed to the retardant by using a 2-hour cycle alternate submersion-immersion machine (2 min retardant exposure; 1 hour 58 min drying period). The U-bend samples will be removed from the retardant after 300 hours of exposure. Two additional U-bend samples will be exposed to the atmosphere for control purposes.

Performance (Intergranular Corrosion 3.1.4.3.): These tests were performed by the San Dimas Equipment Development Center, San Dimas, California. SDEC reported that "there was no intergranular corrosion caused by Fire-Trol 931-L, 931-N, or 931-P." (Data on file at the Northern Forest Fire Laboratory or San Dimas Equipment Development Center.) (Note: Intergranular corrosion tests were only performed on the liquid concentrate and the mixed retardant at the 4:1 dilution rate.)

pH Values (3.1.5.)

Requirements: The pH of the liquid concentrate and "mixed retardant" shall be between 6.0 and 8.0.

Performance: The pH of the concentrate and mixed solutions of Fire-Trol 931-L, 931-N, and 931-P was determined using a Sargent Model LS pH meter (accuracy ± 0.05 pH units). The results given below show that in mix ratios of from 0 parts water with 1 part concentrate to 10 parts water with 1 part concentrate, the pH of all mixtures is between 6.0 and 6.65 except Fire-Trol 931-N concentrate which is 5.82.

Retardant mix ratio (water to conc. by volume)	pH of solution		
	Fire-Trol 931-L	Fire-Trol 931-N	Fire-Trol 931-P
Concentrate	6.10	5.82	6.20
1:1	6.28	6.09	6.33
2:1	6.40	6.19	6.42
3:1	6.43	6.22	6.50
4:1	6.46	6.27	6.51
5:1	6.53	6.32	6.54
6:1	6.52	6.32	6.58
7:1	6.56	6.37	6.59
8:1	6.59	6.39	6.55
9:1	6.53	6.40	6.57
10:1	6.62	6.42	6.65

A plot of the pH as a function of dilution rate (fig. 8), shows a constant decrease in pH from the most dilute to the most concentrated.

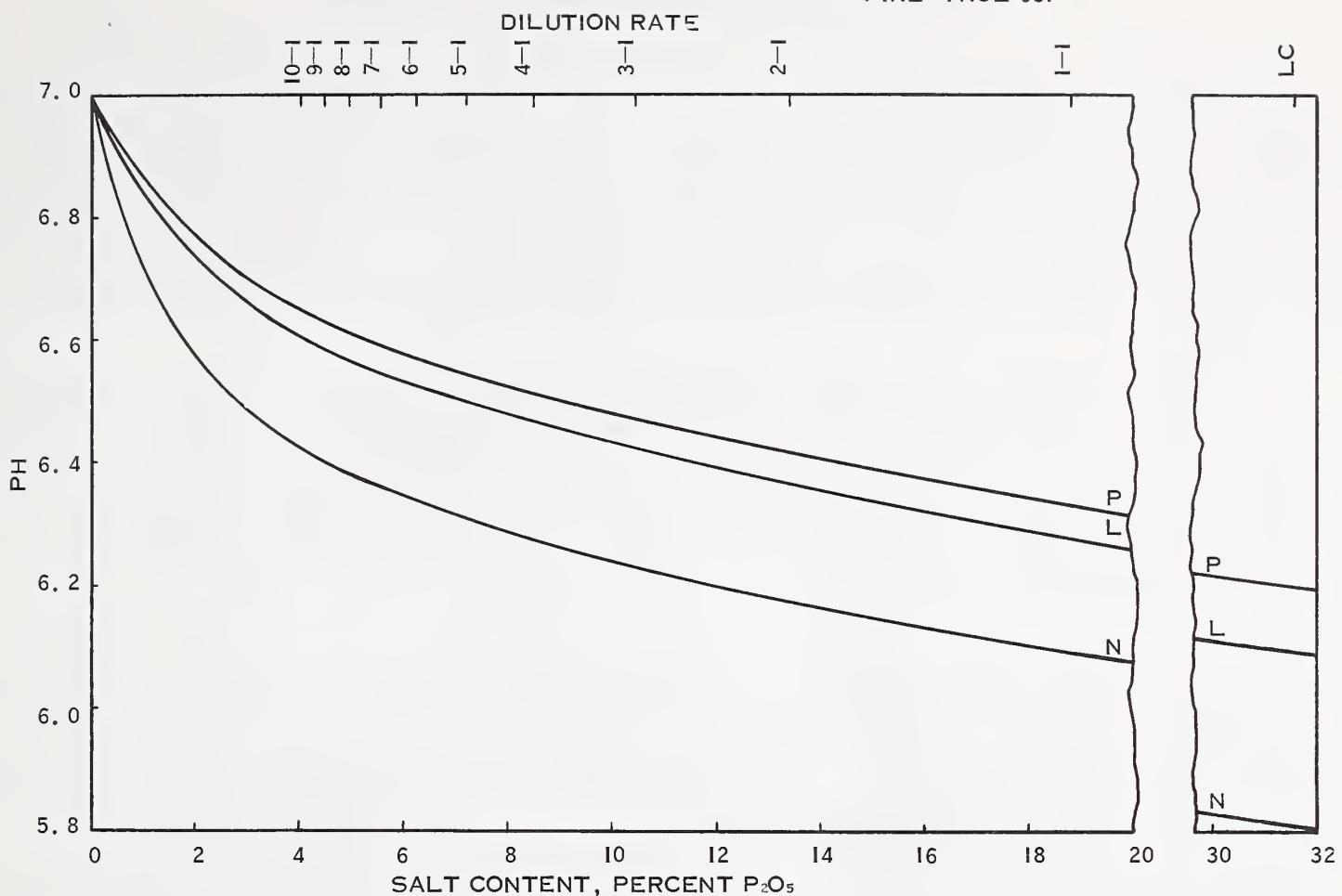


Figure 8.--pH of the retardant solution as a function of dilution rate or salt content.

Abrasion and Erosion (3.1.6.)

Requirements: An aluminum 2024-T3 disc and wear plate will be used to determine abrasion and erosion characteristics of retardant samples. The disc is 4.00 ± 0.01 inches in diameter and approximately 5/16 inch thick, with an overall thickness tolerance of ± 0.001 inch. The wear plate has a similar thickness; but it is square, with an edge dimension that exceeds the diameter of the disc.

The disc will be mounted on a rotating shaft and positioned parallel to and directly above the stationary wear plate. The uniform space between the disc and wear plate will be 0.020 ± 0.001 inch.

With the disc and wear plate immersed about 2 inches into the retardant sample, the disc will be rotated at 1,800 r/min for 50 hours. Thickness measurements will be taken on the plate and the disc with an average thickness determined. Maximum abrasion shall not exceed 0.010 inch.

Performance: These tests were performed by the San Dimas Equipment Development Center (data on file at the Northern Forest Fire Laboratory and San Dimas Equipment Development Center) and their reports show the total measured wear was 0.0085 inch for 931-L, 0.004 inch for 931-N, and 0.0095 inch for 931-P. All three retardants had less than the maximum allowable 0.010 inch and are, therefore, acceptable.

Apparently only the mixed retardant at a 4:1 dilution ratio was tested. Although the performance of the concentrate and other dilutions is not known, similar performance for these solutions will be required.

Combustion Retarding Effectiveness (3.1.7.)

Requirements: The long-term fire-retarding effect of the retardant will be measured by burning ponderosa pine needle and aspen excelsior fuel beds treated with the mixed retardant. The 8-foot-long, 18-inch-wide, 3-inch-deep fuel beds will be prepared to reproducible specifications using 6 pounds of needles or 4 pounds of excelsior that have been predried to a 5.0 to 7.5 percent equilibrium moisture content. The mixed retardant will be sprayed uniformly into fuel beds at 1 and 2 gal/100-ft² levels and then dried until 100 percent of the original moisture has evaporated. The treated beds will then be burned under controlled conditions of 90° F, 20 percent relative humidity, and in a 5 mi/h wind.

The parameters used to determine retardant effectiveness will be rate of fire spread and fire intensity. The rate of spread (Rs) will be measured visually as the flame front moves through the treated fuel. Fire intensity will be determined by measuring fuel rate of weight loss (Rw) during the fire and the residue weight (Rr) after all combustion has stopped. The reduction in spread and intensity rates caused by the retardant treatment will be determined as a percent of untreated values for the same parameters in similar fires.

The retardant will be evaluated by use of a numerical rating called a superiority factor (S.F.). The percent reduction data from all fires will be combined, weighted, and calculated into one numerical factor that can be used to compare a given product to any other tested product. The superiority factor is a numerical index from 0.0 to 1.0. A chemical registering an S.F. of 0.0 would have no retarding effect and a chemical having an S.F. of 1.0 would prevent combustion.

The overall superiority factor is calculated for both fuel types, application rates, and parameters measured by the formula. The equation used to compute superiority factors for each retardant is:

$$\begin{aligned} S.F. = & 0.25 (\% \text{ decrease } Rs \text{ needles}) + 0.25 (\% \text{ decrease } Rs \text{ exc}) \\ & + 0.125 (\% \text{ decrease } Rw \text{ needles}) + 0.125 (\% \text{ decrease } Rw \text{ exc}) \\ & + 0.125 (\% \text{ reduction in fuel consumed needles}) \\ & + 0.125 (\% \text{ reduction in fuel consumed exc}). \end{aligned}$$

For a retardant to be considered effective, its superiority factor, plus the standard error of the mean, must fall between 0.50 and 1.00. (This deviates from the acceptable level of 0.60 given in USDA specifications 5100-00301 and 5100-00302a. The lower acceptance level occurs because an additional fire intensity parameter (residue or fuel consumed) has been added to the superiority factor calculation, thus causing a reduction of approximately 0.10.)

Performance: The superiority factors for Fire-Trol 931-L, 931-N, and 931-P as a function of the amount of chemical applied are shown in figure 9. (The actual data from which the superiority factors were derived are given in appendix C.) Figure 9 also shows the standard DAP superiority factor (George and Blakely 1972) as a function of the grams of P₂O₅/ft². To assure comparability of data establishing the standard curve with the fuels and conditions used for evaluating the Fire-Trol APP products, tests using standard DAP solutions were also conducted. The results from these fires are shown as "DAP" points and are shown to fit the previous standard DAP curve very well.

Although the average values for superiority for all parameters, fuels, and concentration levels combined closely fit the standard DAP curves, individual elements often contain significant variation. (See figures in appendix C.) However, the general difference between the Fire-Trol APP solutions and the "DAP" are quite consistent.

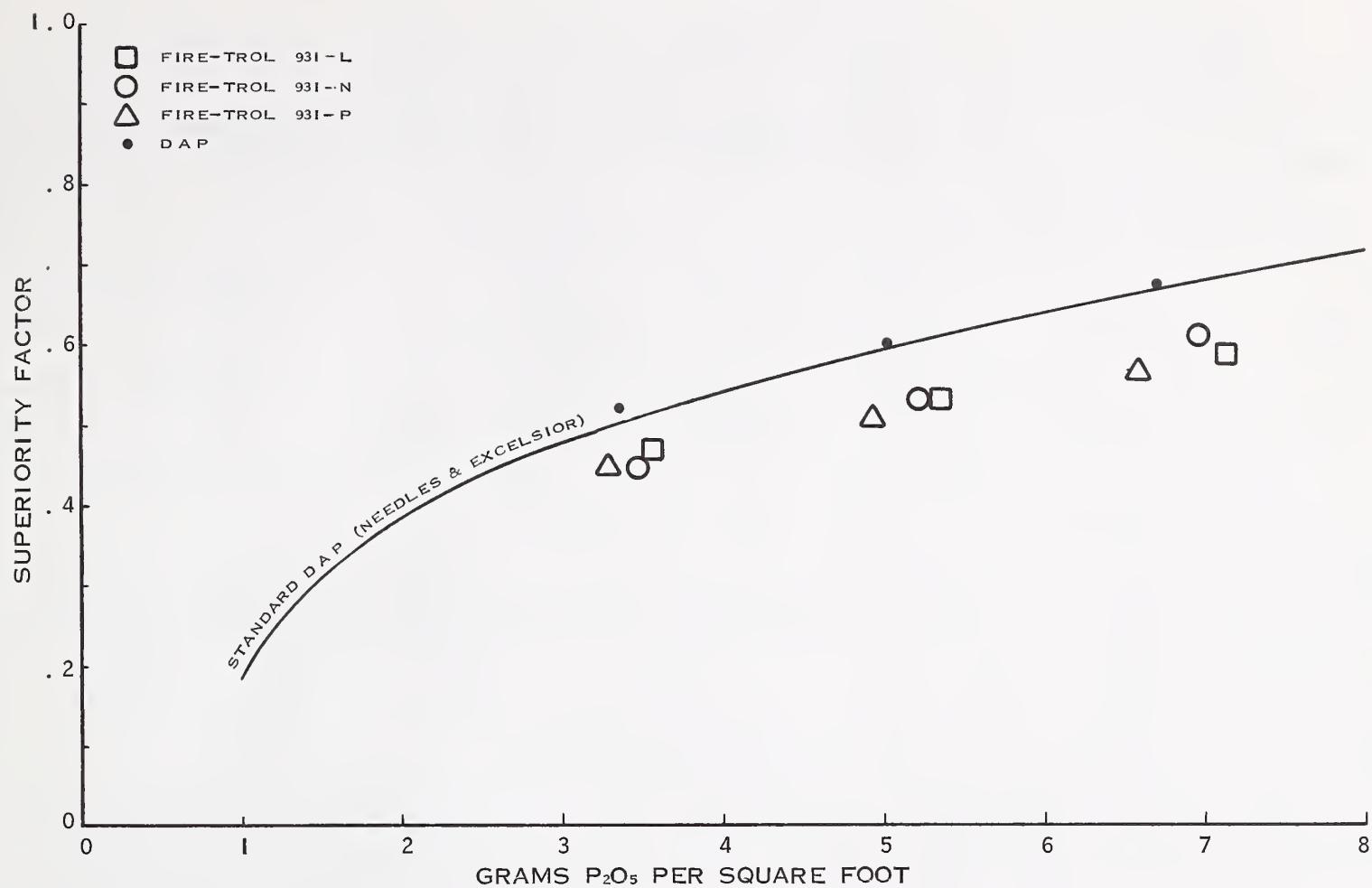


Figure 9.--The superiority factor for Fire-Trol 931-L, 931-N, 931-P, and standard DAP as a function of the amount of chemical applied.

The difference in effectiveness between Fire-Trol 931 APP products and DAP solutions is primarily due to the presence of impurities in Fire-Trol; however, small differences might be attributed to the form and availability of the P₂O₅ (ortho vs. polyphosphate content). Basic green acid 10-34-0 solutions contain small percentages of impurities (table 7) and can tie up the phosphate to form insoluble compounds that may or may not be effective fire retardants. Usually, compounds formed with Fe, Ca, and Mg are ineffective due to their high temperature requirement for decomposition and thus their unavailability especially in terms of altering pyrolysis and combustion reactions.

The data below show the relative efficiency in terms of effectiveness for the Fire-Trol APP and DAP solutions.

(All treatments, levels, and fuels)	Superiority factor	
	(Equivalent DAP solution)	
Fire-Trol 931-L	0.53	0.60
Fire-Trol 931-N	.53	.59
Fire-Trol 931-P	.51	.57

Table 7.--Results of chemical analysis of Fire-Trol 931-L, 931-N, and 931-P

Element	Method ¹	Liquid concentrate			Mixed 4:1		
		931-L	931-N	931-P	931-L	931-N	931-P
- - - - - Percent by weight - - - - -							
N	1	9.29	9.30	9.30	2.51	2.50	2.50
P ₂ O ₅	1	31.58	31.62	31.62	8.52	8.51	8.49
N	2	9.90	9.69	9.45	2.46	2.55	2.60
P ₂ O ₅	3	31.75	30.00	29.40	8.49	8.28	7.82
- - - - - p/m - - - - -							
Zn	4				30	67	136
Mn	4				30	7.5	12.5
Cu	4				6.5	8.0	16.5
Fe	4				4,863	5,050	5,013
Ca	4				70	61	64
Mg	4				272	176	279
Cr	4				41	66	87
Pb	4				1.5	1.9	2.4
Cd	4				2.5	1.3	16.2
Ni	4				6.0	2.75	16

¹Method:

1. Calculated from manufacturer's data
2. Micro-Kjeldahl analysis
3. Colorimetric analysis
4. Commercial lab (USTL, Inc.)

In other words, to compare effectiveness, the comparison must be made on more than just the total P₂O₅ equivalent, since the P₂O₅ may or may not be available. For example, the level of phosphate in Fire-Trol 931-L reduced combustion by 53 percent over untreated fuel. Had the same phosphate been "available" as in the DAP solution tested, it would have reduced combustion by 60 percent.

Fire-Trol 931-L, 931-N, and 931-P have a superiority factor of 0.53, 0.53, and 0.51, respectively, when mixed at a 4:1 dilution rate, which is greater than the minimum allowable superiority factor (0.50). However, in dilutions of more than 4:1, the superiority factor will fall below the 0.50 level.

Color (3.1.8.)

Requirements: Type A, air applied, liquid concentrate shall contain sufficient nonstaining coloring agent so that the "mixed retardant" shall contain a minimum of 16 grams of coloring agent (Fe₂O₃) per mixed gallon or equal. Color for type G, ground applied, liquid concentrate is optional. If color is specified, type G liquid concentrate shall contain sufficient nonstaining coloring agent so that the "mixed retardant" shall contain a minimum of 5 grams of coloring agent (Fe₂O₃) per mixed gallon or equal.

Performance: The color composition of each of the Fire-Trol APP solutions is given in appendix A. Using the composition given, the quantity of coloring agent was calculated and is given below:

	<i>Coloring agent</i>	<i>Quantity (Grams/gallon of mixed retardant)</i>
Fire-Trol 931-L	Dye	--
	Fe ₂ O ₃	16.15
Fire-Trol 931-N	Dye	--
	Fe ₂ O ₃	16.12
Fire-Trol 931-P	Dye	--
	Fe ₂ O ₃	16.18

Thus, Fire-Trol 931-L, 931-N, and 931-P when mixed at a dilution rate of 4:1 contain at least 16 grams of coloring agent (Fe₂O₃) as required.

Health and Safety (3.1.9.)

Requirements and Performance: USDA specifications 5100-00301 and 5100-00302a contain no requirements for health and safety. However, evaluation procedures usually include review of the composition and a literature search of toxicity information concerning these compounds.

In the case of the Fire-Trol 931 APP formulations, the toxicity of the basic ingredient (10-34-0) is fairly well documented. A partially completed literature review conducted by George (results on file at the Northern Forest Fire Laboratory) and recent studies by the National Marine Fisheries (Blahm and others 1974), indicated and substantiated that the primary environmental impact of the APP solutions is their effect on water quality and marine life. Low concentrations can be toxic to fish and other aquatic organisms. The NH₃ has been determined to be the toxic ingredient and, because of the relative amount of NH₃ contained in the formulations, will usually overshadow the effect of the minor ingredients contained in the formulation. A study by the Pacific Northwest Forest and Range Experiment Station is determining the effects of streamside application of ammonia-based fire retardant on streamwater chemistry and benthic organisms (Study Plan 1602-54, Pacific Northwest Station. Data on file at the Northern Forest Fire Laboratory).

The possible effects of the retardant on human health have been a concern. For example, in the Pacific Northwest Region sodium dichromate corrosion inhibitor was removed from Fire-Trol 931 for operational use after The Dalles (Oregon) City Water Board became concerned about the toxic effects of the sodium dichromate.

When Fire-Trol 931-L was submitted with sodium ferrocyanide as a corrosion inhibitor, the "ferrocyanide" cast some doubt on "health and safety" effects. A thorough literature review and laboratory tests were performed to determine the legitimacy of such doubts and establish what effects might be expected. (Data on file at the Northern Forest Fire Laboratory.) Truesdial Laboratories conducted independent tests and determined that when ferrocyanide was burned, most of the cyanogens became CO₂ rather than poisonous HCN gas. When retardant is applied on wildfires at 2 gal/100 ft², the maximum possible HCN given off is 50 mg/m³ total. Since OSHA allows a maximum exposure level to HCN gas of 11 mg/m³ in air during a 40-hour work week, no harmful human or environmental effects are expected.

Mixing (3.1.10.)

Requirements: The mixing of unthickened liquid retardants shall be simply by adding water to the liquid concentrate. For thickened liquid retardant the slurry shall reach the accepted viscosity within 4 minutes' mixing time (as prescribed in the "thickened" specification 5100-00301). The accepted viscosities are:

	<u>Viscosity</u> (cP)
Gum-thickened retardants (type I)	1,000-2,000
Gum-thickened retardants (type II)	1,500-2,500

Performance: The Fire-Trol 931 APP products can be mixed simply by adding water. However, agitation is required for the solution to be adequately mixed--the active retardant salt evenly distributed throughout the solution. The gum-thickened Fire-Trol 931 APP solutions also require shear or agitation to evenly distribute the low concentration of gum within the diluted APP solution. Obtaining a good uniform quality of the mixed retardant (both salt and viscosity) is a function of the mixing system being used. The performance of the gum in developing the required viscosity is covered in section 3.1.3. (viscosity). The viscosity of the gum-thickened Fire-Trol 931-L does not reach the accepted level in 4 minutes as required in the thickened retardant specification; however, it does reach this level in approximately 15 minutes (probably acceptable performance). Only a few comparative tests were run on hydration times for gum-thickened Fire-Trol 931-N and 931-P, but they showed similar results to the 931-L tests.

Salt Content (3.1.11.)

Requirements: Standard chemical analysis procedures will be used to analyze each liquid concentrate for phosphorous and nitrogen content. A colorimetric method will be used for determining the P_2O_5 (P) equivalent in all ammonium phosphate solutions. A micro-Kjeldahl distillation method will be used to analyze for NH_3 (N) in all ammonium compounds.

To analyze for P_2O_5 , a sample (the size depending on the apparent P_2O_5 equivalent) will be digested by a wet process using ternary acid to dissolve all ingredients. To this sample is added perchloric acid and ammonium molybdate. Amino-naphthol-sulfonic acid is then added, and color is allowed to develop for 10 minutes. The optical density at $660\text{ m}\mu$ versus a reagent blank is then read, using a Beckman DU spectrophotometer. Using a standard curve, the percent P in the sample can be calculated and the percent P_2O_5 determined.

To analyze for ammonia, samples of the retardant are weighed to ± 0.1 milligram, placed in the distillation apparatus, and the ammonia boiled off and captured in a boric acid solution. The solution is titrated with dilute hydrochloric acid of a known molarity, and the ammonia is calculated and the percent N determined.

The P_2O_5 equivalent salt content of the liquid concentrate shall not be less than 30 percent. After a sample has been stored for 1 year as specified above (3.1.1.), the salt content shall be within ± 3 percent of that determined before storage..

Performance: Liquid concentrates of Fire-Trol 931-L, 931-N, and 931-P were analyzed using both the colorimetric and micro-Kjeldahl methods to determine their P₂O₅ and N content. The salt content of the Fire-Trol 931 formulations and the methods used for analysis are given below:

	931-L	931-N	931-P
Percent P ₂ O ₅ , theoretical	31.58	31.62	31.62
Percent P ₂ O ₅ , colorimetric	31.75	30.00	29.40
Percent N, micro-Kjeldahl	9.90	9.69	9.45

All three concentrate formulations meet the requirement for 30 percent P₂O₅ when determined by using the manufacturer's theoretical data. When analyzed by the colorimetric method, 931-L and 931-N meet the requirement but 931-P, containing 29.40 percent P₂O₅ content, falls slightly below the required concentration. This, however, is probably not significant unless the retardant combustion effectiveness (superiority factor) falls below the accepted level.

The salt content of Fire-Trol 931-P as a function of dilution rate and specific gravity was given in Section 3.1.2. (specific weight). For quality control purposes in the field it can be assumed, as discussed, that Fire-Trol 931-L and 931-N are similar to 931-P (in other words, use the same calibration table for these three formulations).

When checks were made for "salting out" of 931 formulations stored over an 8 to 18 month period, salt concentration had not changed.

Separation (3.1.12.)

Requirement: Two quarts of liquid concentrate will be mixed to the manufacturer's recommended proportions and placed in unsealed (loosely covered) glass quart jars. The concentrate will sit undisturbed for 1 year, be inspected periodically, and the separation of components measured and recorded. Two quarts of freshly mixed retardant will also be placed in glass jars and sit undisturbed for 4 hours. The separation of components will be measured with a linear scale and recorded every 15 minutes. Neither the liquid concentrate nor the mixed retardant shall display any visual division of one or more components (for example, the thickening agent, coloring agent, etc.) within the sample amounting to more than 5 percent by volume.

Performance: Fire-Trol 931 APP products are designed to be diluted to different concentrations on demand; therefore, separation tests were performed using several dilutions of the three concentrates: Fire-Trol 931-L, 931-N, and 931-P. The formulations were tested unthickened, at dilutions of 2:1, 3:1, 4:1, 5:1, 6:1, and 7:1. The amount of separation occurring following the mixing of the three formulations as a function of time is shown in figures 10 through 16. In the first three figures (10, 11, 12) an expanded scale is used to show the amount of separation prior to the 4 hour period--less than 5 percent separation should occur at that point. Actually, all three products separate to a greater extent than allowed--depending on the dilution.

Figures 13, 14, and 15 show the extent of separation during storage up to 40 days. In general, the separation rate decreases after several days (approximately 4 days for 4:1 dilutions) and the total separation is from 40 to 60 percent shortly thereafter.

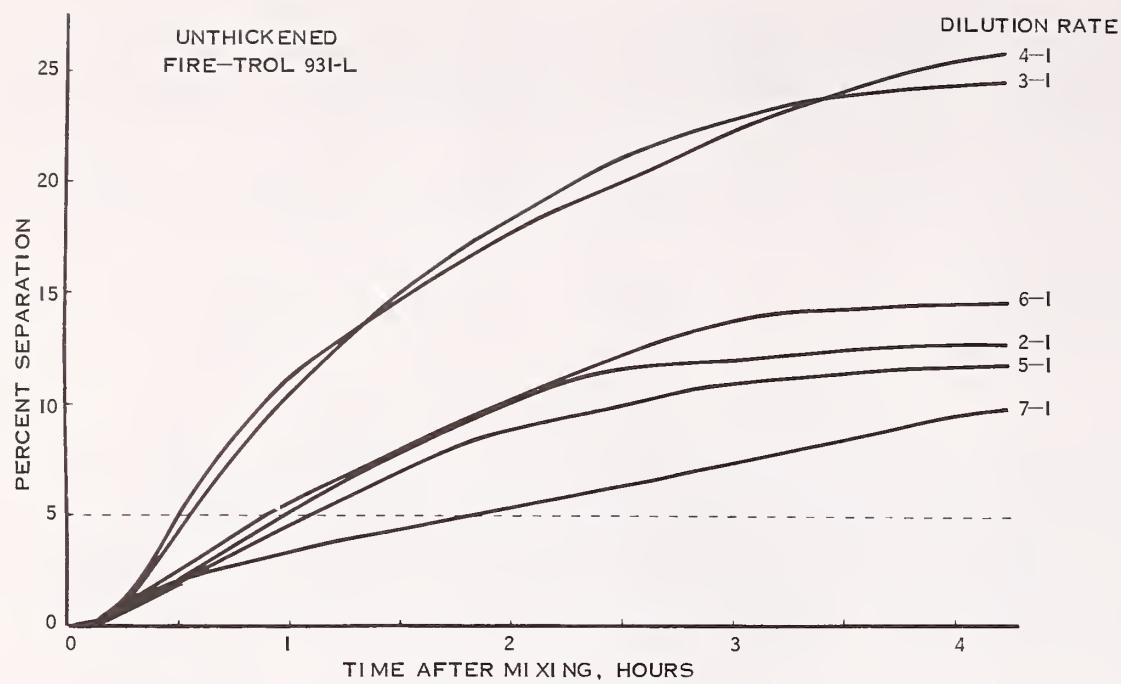


Figure 10.--Separation of unthickened Fire-Trol 931-L as a function of time after mixing.

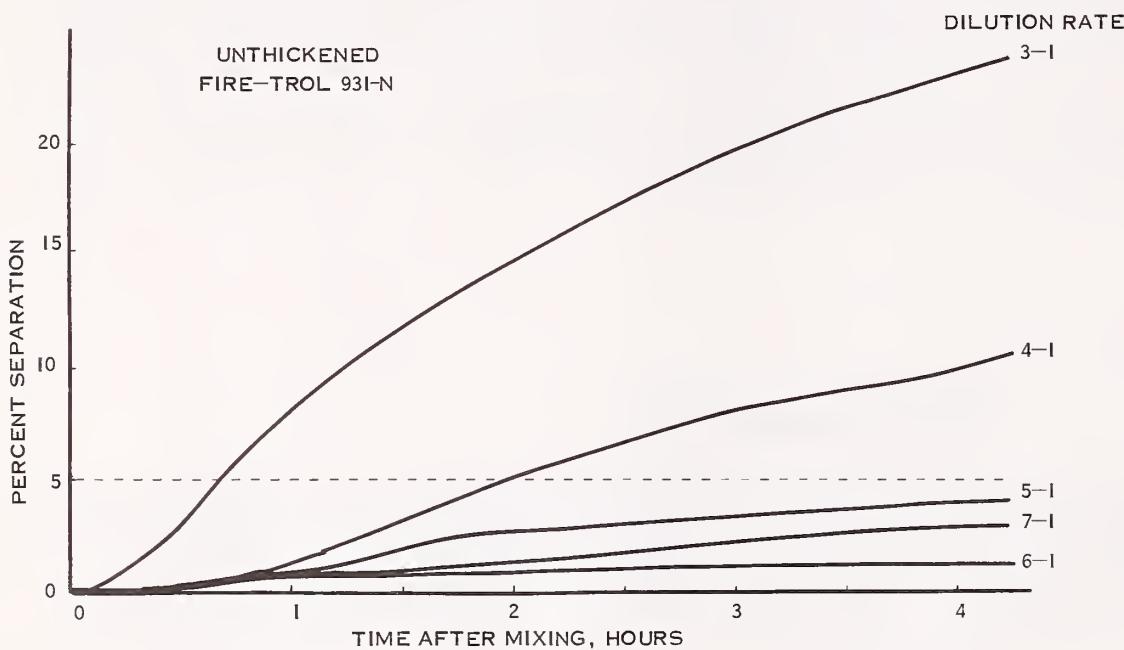


Figure 11.--Separation of unthickened Fire-Trol 931-N as a function of time after mixing.

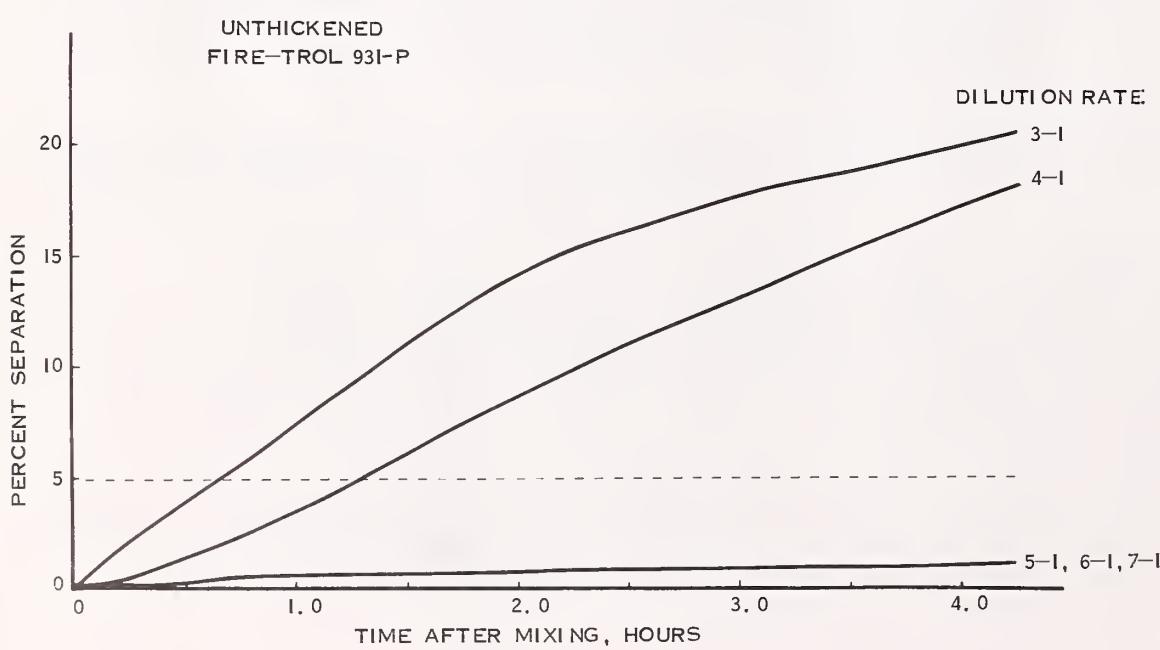


Figure 12.--Separation of unthickened Fire-Trol 931-P as a function of time after mixing.

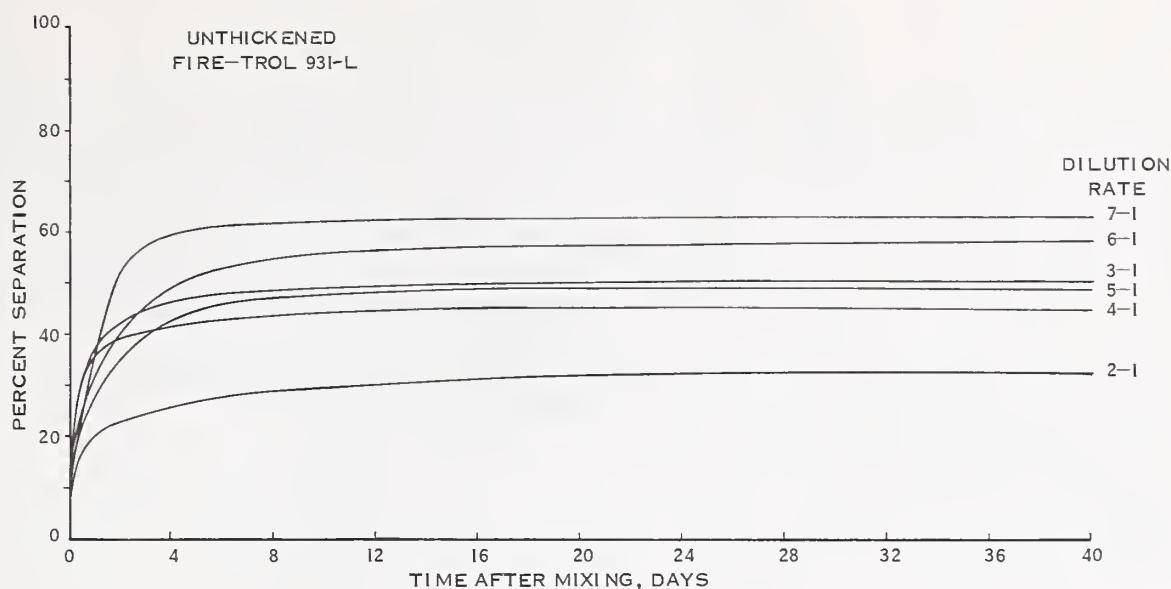


Figure 13.--Long-term separation of unthickened Fire-Trol 931-L as a function of time after mixing.

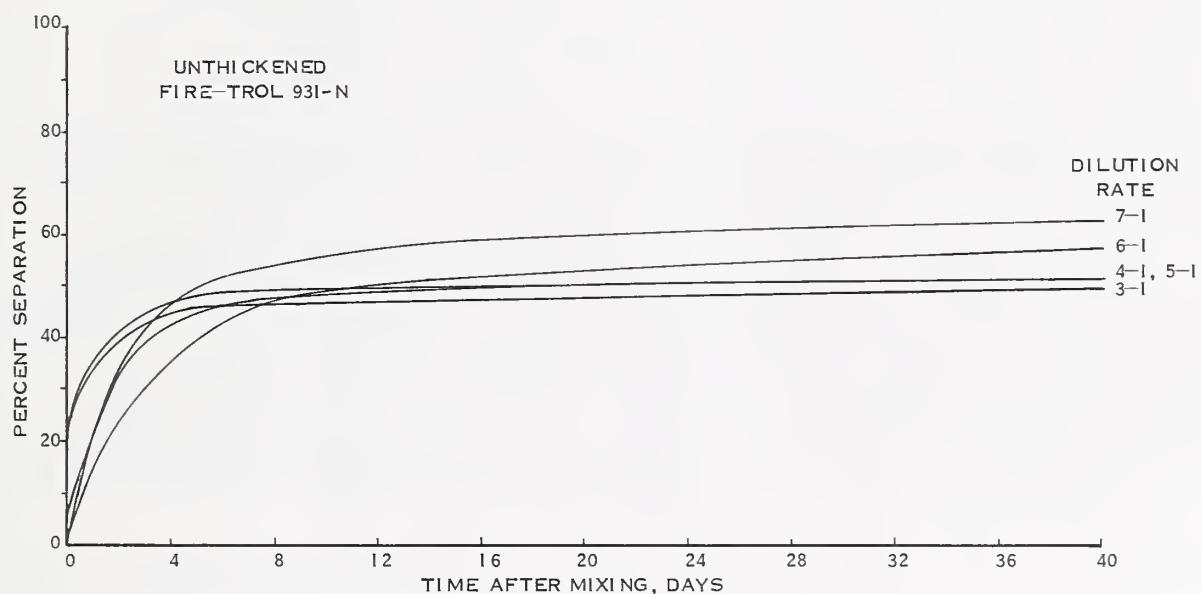


Figure 14.--Long-term separation of unthickened Fire-Trol 931-N as a function of time after mixing.

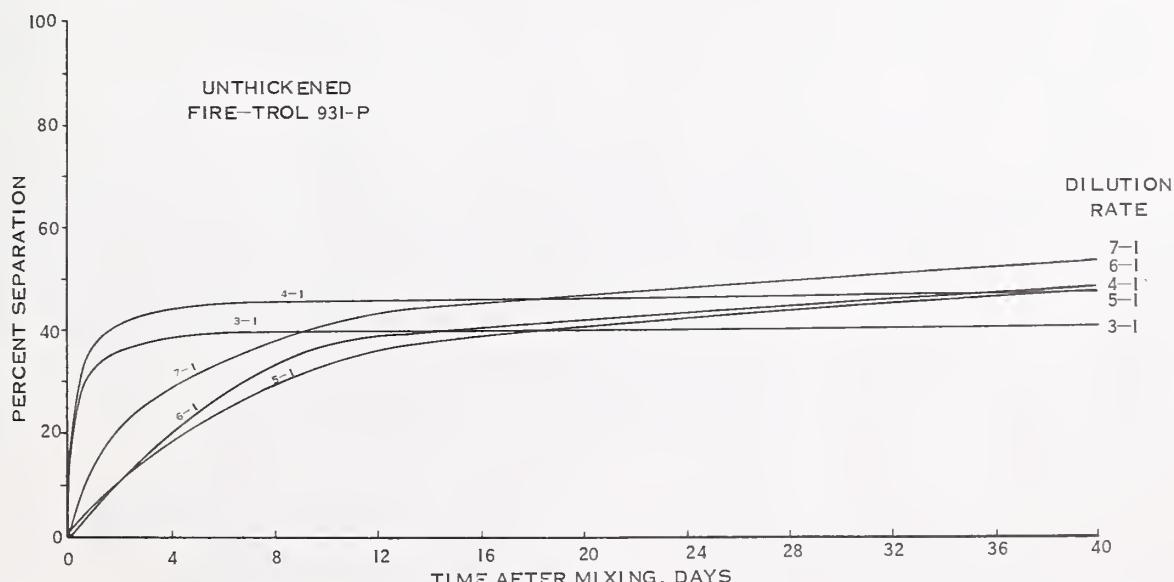


Figure 15.--Long-term separation of unthickened Fire-Trol 931-P as a function of time after mixing.

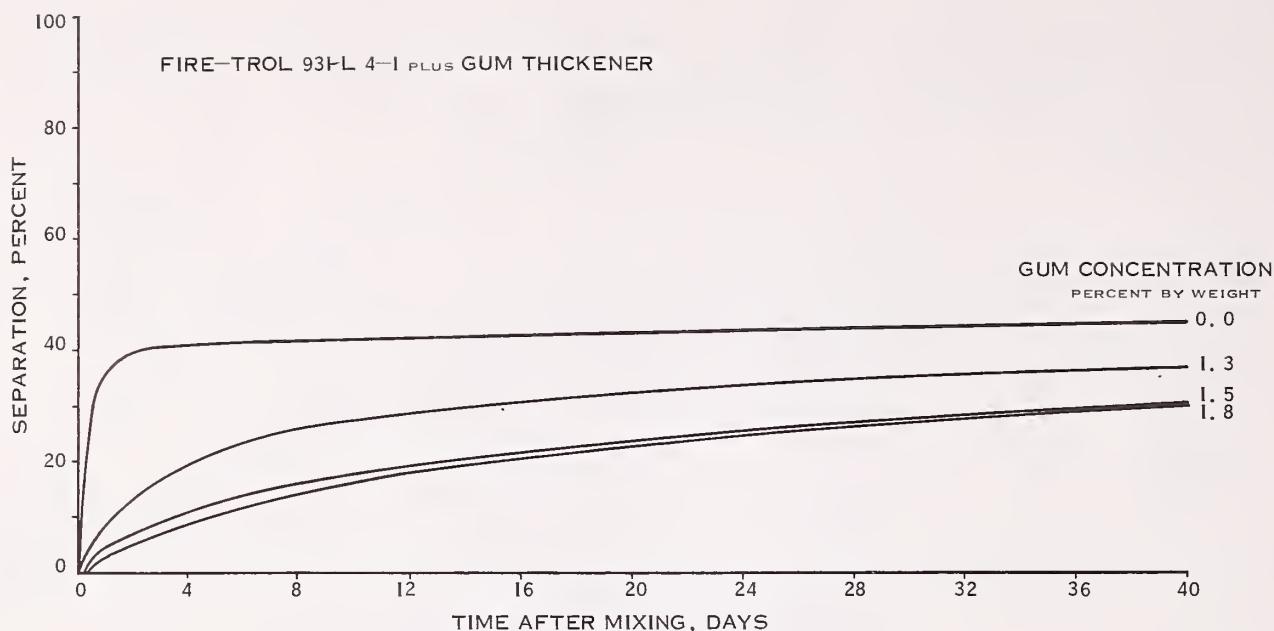


Figure 16.--Separation of gum-thickened Fire-Trol 931-L as a function of time after mixing.

Separation occurring at various time intervals for the several formulations is given below:

Dilution rate	Time following mixing	Percent separation (by volume)
		Fire-Trol 931-L : Fire-Trol 931-N : Fire-Trol 931-P

4:1	1 h	11	10	3
	11 4 h	25	23	17
	1 d	38	32	39
	7 d	48	50	46
	14 d	52	51	46

1.5 percent gum-thickened Fire-Trol 931-L

4:1	4 h	0
	1 d	5
	7 d	16
	14 d	20
	30 d	30

The only gum-thickened formulation evaluation for separation was Fire-Trol 931-L diluted at 4:1 with several concentrations of gum thickener. At all gum concentrations separation occurred gradually, reaching 20 percent after 2 weeks and approximately 30 percent after 1 month (fig. 16). It is interesting to note that separation occurred to a greater extent than would be expected on the basis of the solution's viscosity (Viscosity section 3.1.3., figures 3-6). Therefore, diluted 931-L, with or without thickener, does not fulfill the requirements for separation.

¹¹ Required performance at 4 hours is <5 percent separation (by volume).

Spoilage (3.1.13.)

Requirements: One gallon of liquid concentrate will be placed in four 1-quart jars. A 25 cc specimen from a culture of aerobacter bacteria will be added to two of the samples without stirring or agitation. The four samples will be stored unsealed (loosely covered) under ambient conditions at 75-85° F. The samples will be visually checked and the viscosity measured at weekly intervals for a 3-month period. Separation of more than 5 percent, or a decrease in viscosity, constitutes spoilage. Growth of mold or an unpleasant odor is also considered spoilage.

Performance: Samples of unthickened Fire-Trol 931-L, 931-N, and 931-P were diluted at 3:1, 4:1, 5:1, 6:1, and 7:1, and insulted with bacteria. These were visually inspected for growth of mold and rate of separation. Because of the naturally occurring separation, it was not meaningful to determine the viscosity weekly--since this would require agitation of the sample and the insult bacteria. Fire-Trol 931-L, 931-N, and 931-P took about 1 1/2 months before spoilage was evident to an extent that the materials would not meet the requirements. The 3:1 dilutions of Fire-Trol 931-N were the first samples to show mold growth and give off a pungent odor.

Samples of gum-thickened Fire-Trol 931-L were similarly insulted with a bacteria. All gum-thickened samples promoted mold growth, with an increasing separation rate. Spoilage began at irregular initiation periods, as early as 3 days after being insulted. The initiation period for spoilage probably depends on the number of bacteria in the insult, which could not be controlled, as well as many other factors. Although there is no specification for thickened liquid base retardants, operational use is not recommended for a material having these spoilage characteristics and thus viscosity degradation.

The San Dimas Equipment Development Center tested for spoilage (data on file at the Northern Forest Fire Laboratory and San Dimas Equipment Development Center), with Fire-Trol 931-N and 931-P concentrates and 4:1 mixtures. Both solutions of each formula supported the bacterial culture, as evidenced by an unpleasant odor and mold growth where the culture was at the surface of the liquid. However, the culture did not degrade either the concentrate or the "mixed retardant."

Pumpability (3.1.14.)

Requirements: For retardants with non-Newtonian flow characteristics, an electric pump (flow model Mac X-3, 220 volt, 3 phase, 3/4 horsepower, 2,580-3,450 r/min) with a 1-inch inlet and outlet and a cast iron impeller will be used. The pump will be run at 3,400 r/min to transfer liquid concentrate from a holding tank to a weighing tank. Standard procedures will be used to monitor the pump r/min and the weight of retardant in the weighing tank. These procedures will be performed five times for each different sample. The rate of weight increase and the specific weight of the retardant will be used to determine the flow rate in gallons per minute. A minimum flow rate of 12 gal/min must be obtained.

For retardants with Newtonian flow characteristics, the kinematic viscosity for the material will be computed using density and viscosity:

$$\frac{\text{viscosity (cP)}}{\text{density } \left(\frac{\text{g}}{\text{cm}^3} \right)} = \text{centistokes}$$

The retardant shall not exceed 1,800 centistokes.

Performance: The tests, performed by the San Dimas Equipment Development Center (Pickett 1975), showed that Fire-Trol 931-L concentrate meets performance requirements (data on file at San Dimas Equipment Development Center and Northern Forest Fire Laboratory). Because some components separated, two separate centistoke tests were conducted. Material from the bottom of the barrel was calculated at 3,015 and 3,103 centistokes, and material from the top of the barrel at 1,055 centistokes. (The maximum acceptable level is 1,800.)

On four test runs the 931-L concentrate was pumped in excess of 12 gal/min (the minimum allowable) and in one test at 9.5 gal/min. The average, 13.4 gal/min, was considered acceptable. It was noted during the tests that the pump could not be primed with the Fire-Trol 931-L concentrate.

In pumpability tests Fire-Trol 931-N had an average flow rate of 9.1 gal/min and a maximum of 10.3 gal/min, both below the required 12 gal/min. Therefore, pumpability of the retardant is unacceptable.

Fire-Trol 931-P could not be pumped because of crystals formed when the concentrate salted out. (The retardant had a 0.6 percent decrease in salt content because of the "salting out.") SDEDC recommends disqualifying 931-P because of the possible serious abrasion to pumps or other hardware used at air tanker bases.

Air Drop Characteristics (3.1.15.)

Requirements: For aircraft-applied-type retardant the liquid concentrate will be mixed at the manufacturer's recommended level and dropped from a TBM-type air tanker. The air tanker will have a tank and gating system with two gates, each being 9 by 136 inches. Aircraft speeds will be held at 105-115 knots, temperature 60-90° F, relative humidity 20-60 percent, and <5 mi/h wind. For a load of 600 gallons dropped from 200 (± 20) feet and with a wind of 5 mi/h or less:

1. 60 percent (400 gallons) or more of the retardant shall fall within the total pattern area.
2. The area covered by ≥ 2 gal/100 ft² must be $\geq 4,000$ ft².
3. The 2 gallons per 100-ft² area must have a continuous length of >150 ft.

Performance: Because the drop performance of unthickened Fire-Trol 931-D had previously been quantified under the conditions that are specified for this evaluation, and because insignificant differences exist in the drop characteristics of Fire-Trol 931-D and other similarly formulated Fire-Trol 931 products (containing 10-34-0, attapulgite clay, coloring, and corrosion inhibitors, and diluted 4:1; i.e., Fire-Trol 931-L, 931-N, 931-P), the performance data were taken from previous drop tests at Porterville, California. These tests were reported in "An evaluation of the drop characteristics and ground distribution patterns of forest fire retardant" (George and Blakely 1973).

In that analysis, performance models were developed based on the actual drop data, which predicted retardant recovery and area of coverage by concentration class. Fire-line length at the 2 gal/100 ft² coverage level was given for each drop. Utilizing

these data, the performance of Fire-Trol 931-D at the conditions specified under requirements is given below:

<i>Requirement</i>	<i>Performance of Fire-Trol 931-D</i>
Recovery: 60 percent of total load or 400 gal	550 gal at 0 mi/h wind 427 gal at 5 mi/h wind
Area of coverage at ≥ 2 gal/100 ft ² $\geq 4,000$ ft ²	9,264 ft ² at 0 mi/h wind 4,802 ft ² at 5 mi/h wind
Length of fireline ≥ 2 gal/100 ft ² >150 ft	~ 208 ft ¹²

Note that the predictions for water dropped under the same conditions also meet all the requirements listed above.

In late 1973, gum-thickened and petrolite-thickened Fire-Trol 931-L were submitted to the Forest Service (NFFL) for evaluation. In January 1974, cooperative agreements were made between the USDA Forest Service (Northern Forest Fire Laboratory) and Chemonics Industries to perform laboratory tests and actual drop tests with the two formulations. This study was initiated in February 1974, at Marana, Arizona. A B-17 was selected as the test aircraft rather than the TBM as specified in the requirements for two reasons:

1. The TBM was dropped from operational use as an approved air tanker in 1974.
2. Previous tests, investigating the effect of retardant rheological properties on drop characteristics, had been conducted using the B-17 (Intermountain B-17, No. 71) and provided a data base for these tests--thus reducing the number of required drops.

During these tests, 44 drops of 466 gallons each (1 compartment) were made and the ground distribution patterns analyzed.¹³

Preliminary analysis of these data has been completed and the following conclusions drawn:

1. The drop performance of the unthickened Fire-Trol 931-L is vastly improved by the addition of the gum-thickening agent or the Petrolite inverter. The gum-thickened retardant, however, is superior to the Petrolite emulsion and has the advantage that the concentration of the gum can be controlled to allow selection of a much wider range of retardant rheological properties.
2. The optimum viscosity of the gum-thickened retardant appears to be near 2,000 centipoise. At higher viscosities (3,000 cP) the areas of coverage tended to be reduced (especially at the lower drop heights). At higher drop heights (greater than 300 ft) and coverage levels (3 or 4 gal/100 ft²), however, there may be advantages for APP solutions having viscosities near 3,000 centipoise.

¹² Determined as an average of all drops from 200 ft or less and with ≤ 5 mi/h winds (total number of drops = 10, S_d = 25 ft, S_m = 8 ft).

¹³ George, C. W. 1974. Evaluation of the drop characteristics of two thickened liquid concentrate fire retardant systems, INT Study Plan 2107-17G, Intermt. For. and Range Exp. Stn., Ogden, Utah.

The differences between unthickened and gum-thickened retardant and also the effects of the gum-thickened retardant viscosity can be determined by comparing the areas of >2 gal/100 ft² coverage in figure 17. Similar conclusions can be drawn from other ground distribution pattern parameters (such as retardant recovery and fireline lengths--figure 18).

Further analysis will be required to correlate levels of performance using the B-17 as a delivery platform, with the requirements specified using the TBM. It can be assumed, however, that the gum-thickened and Petrolite-thickened retardants greatly exceed the performance levels required (based on performance comparisons between unthickened Fire-Trol 931-L and other retardants dropped from TBM and B-17 air tankers).

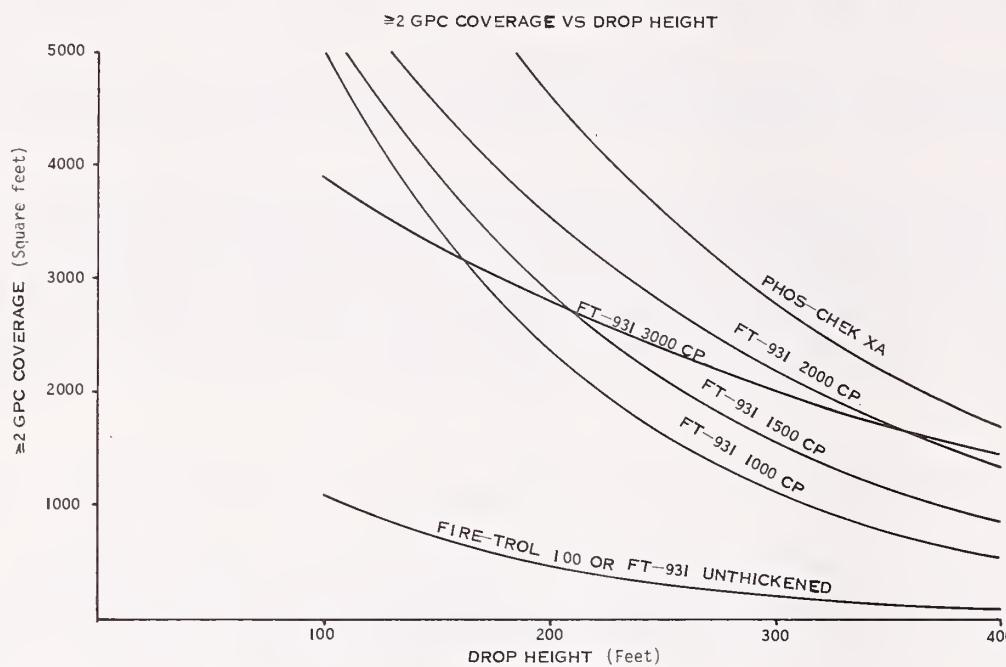


Figure 17.--Comparison of the area of coverage at 2 gal/100 ft² for drops of several viscosities of gum-thickened Fire-Trol 931-L, unthickened Fire-Trol 931-L, Fire-Trol 100, and Phos-Chek XA, as a function of drop height.

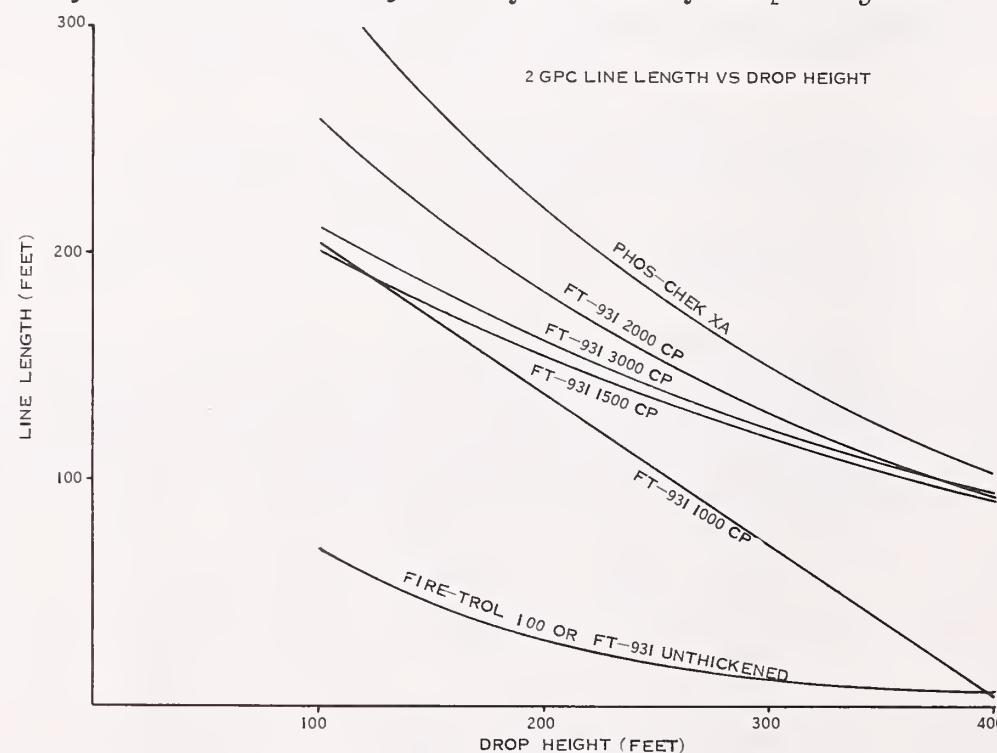


Figure 18.--Comparison of the length of fireline >2 gal/100 ft² for drops of several viscosities of gum-thickened Fire-Trol 931-L, unthickened Fire-Trol 931-L, Fire-Trol 100, and Phos-Chek XA, as a function of drop height.

DISCUSSION

Several Fire-Trol 931 APP formulations (appendix A) were submitted for screening and testing by Chemonics Industries. Although preliminary tests have been performed on a number of these formulations, primary emphasis in this report has been placed on the performance of Fire-Trol 931-L, 931-N, and 931-P, gum-thickened solutions of Fire-Trol 931, and Petrolite emulsions of Fire-Trol 931. A number of dilutions of each of the concentrations were tested because of the flexibility to tailor the retardant solution to specific needs--independent selection of salt content and viscosity. The series of tests were conducted as closely as possible to procedures outlined in USDA Interim Specifications 5100-00301 and 5100-00302a. The formulations discussed were primarily designed for air application and were evaluated accordingly.

It has been stated and emphasized in this report that there is no current specification for thickened liquid-type fire retardants and that some of the requirements may not be totally appropriate. All of the specified tests were conducted, plus several additional tests; however, a number of test procedures required modification to suit specific situations which were primarily dictated by the characteristics of the individual formulations.

Three general areas warrant discussion beyond that given in the specific test sections: corrosion, stability of the mixed retardant, and retardant drop characteristics.

Corrosion. Fire-Trol 931-L, 931-N, and 931-P formulations, when mixed for use within the dilution rates tested, met the performance required in the specifications (<1 mil/yr on Al-2024-T3) for uniform corrosion. However, Forest Service specifications do not require inhibition of corrosion to common alloys other than aluminum 2024-T3 and do not consider type of corrosion other than uniform corrosion, intergranular corrosion, and pitting tendency (for example, types of corrosion such as crevice, galvanic, and fatigue corrosion are not considered).

A summary of field surveys and laboratory studies conducted by Ocean City Research Corporation (OCRC) (Gehring 1974) indicates that corrosion performance requirements should be broadened to include several other alloys, additional types of corrosion, and specific corrosion tests which will better evaluate corrosion effects. In specific tests quantifying the corrosiveness of Fire-Trol 931-L, OCRC came to several conclusions (appendix B):

1. Fire-Trol 931-L is only mildly corrosive to aluminum alloys (≈ 1 mil/yr by alternate immersion tests).
2. Fire-Trol 931-L is severely corrosive to magnesium and zinc alloys. Fire-Trol 931-L corrodes zinc, magnesium, and galvanized steel at significant rates (>5 mils/yr by alternate immersion tests). Thus, contact of galvanized control cables or magnesium alloys with Fire-Trol 931-L should be avoided.
3. The corrosion inhibitor system in Fire-Trol 931-L does not completely eliminate susceptibility to stress corrosion.
4. The corrosivity of Fire-Trol 931-L can be significantly reduced by the use of additional inhibitors.

Several other conclusions regarding other formulations or basic liquid systems are of interest.

1. Fire-Trol 931-D (sodium dichromate inhibitor) corrodes 2024-T3 aluminum, zinc, and magnesium at significant rates (>5 mils/yr by total immersion tests).
2. Uninhibited ammonium polyphosphate (8.3 percent P₂O₅ equivalent) should never be used as a fire retardant without effective corrosion inhibitor additives.
3. Galvanic corrosion can occur at significant rates (~3 mils/yr) with the use of all inhibited formulations.
4. Pyro (11-37-0) causes severe corrosion on almost all alloys (except stainless steel). Pyro should never be used without corrosion inhibitor additives or coatings.

Although the sodium ferrocyanide corrosion inhibitor in Fire-Trol 931-L, 931-N, and 931-P very significantly reduced the corrosion rate of exposed Al-2024-T3 as compared to the sodium dichromate contained in Fire-Trol 931-D, the sodium ferrocyanide may have undesirable staining effects. The sodium ferrocyanide provides corrosion protection by building up a heavy blue coating on the metal surface. The degree of bluing depends on the type of metal, its surface characteristics, etc. This coloring can be quite difficult to remove. Staining of other surfaces such as concrete ramps, etc., can be expected.¹⁴ This coloring may or may not be a problem depending on specific situations.

Solution Stability. There has been considerable discussion concerning the requirements for stability of mixed retardant, especially a demand-mixed Fire-Trol 931-L. The storage requirement for an unthickened mixed retardant is a 4-hour stability period (separation <5 percent at the end of 4 hours), while for a thickened mixed retardant the solution must maintain stability for a 1-year period. Unthickened Fire-Trol 931 products separate to about 50 percent in less than 4 days depending on conditions (10-25 percent in 4 hours). As formulated with the attapulgite clay and iron oxide, it is likely that significant changes in the formulation would be required to meet present specifications.

The gum-thickened Fire-Trol 931 formulations, although their stability is greatly improved over the unthickened formulations, still undergo significant change following mixing (in terms of both viscosity and separation). A possible way these formulations might be formulated to circumvent this problem is by including the coloring agent in the gum thickener and removal of the clay from the liquid APP solution entirely (since its only purpose is to stabilize or hold the color in suspension). A related problem, however, primarily dependent on the quality and control of the gum and APP characteristics, is the sensitivity of the various ingredients. Data presented in the sections on Viscosity (3.1.3.) indicate that the quality of the gum (storage time is a consideration as well as gum separation since the gum settles within the carrier) and the salt content of the retardant (mixing rates) greatly influence the resulting viscosity and solution stability. Only with very precise control of these variables (including adequate circulation of both the liquid gum and the APP solution) can the properties of the end product be controlled (resulting in a mixed retardant with tailored properties). The experiences at the Boise Air Attack base with the gum-thickened Fire-Trol 931-P system have verified the preceding statements. To date the hardware and formulations have not demonstrated that control of retardant properties has been achieved to the necessary degree (salt content \pm 10 percent, and viscosity \pm 200 centipoise).

¹⁴Sodium carbonate (baking soda) has been used to effectively clean stained concrete pads. From communication with Kathy Lacey of Chemonics Industries.

If retardants were delivered immediately after being loaded into the aircraft, there would be little if any problem with separation. However, in actuality, this does not always occur. A survey of air tankers in six different Forest Service Regions (August 1974) indicated 59 percent of the 73 aircraft surveyed at 47 bases always sit loaded, 43 percent sit loaded occasionally, and only 5 percent never sit loaded. It is questionable whether sitting loaded should be required in any case; however it is a current practice and occurs very frequently during periods of high fire danger.

The type of exposure prevalent to air tankers in the field indicates corrosion and retardant solution requirements are important. As earlier discussed, 25-50 percent separation can occur in a matter of hours or days. If this separation exists at the time a drop is made, it is predicted that 50 percent or greater of the effective portion of the drop will be uncolored. This presents definite problems where tactics require multiple drops be tied together (from more than one aircraft or multiple drop increments from the same aircraft). Figure 19 shows the predicted drop pattern from an entire drop and from portions of the drop, with and without color. These predictions are based on the flow rate for a 500-gallon drop from a B-17 using the flow rate-ground distribution model developed by Honeywell (Swanson and Helvig 1973). Thus, it would be highly desirable to have a stable retardant solution with the color uniformly distributed throughout. Similarly, based on current practices, it is desirable and not unreasonable to have retardant solutions that maintain stability (color and viscosity) after being mixed, for a period of at least 2 weeks and preferably a month. Air tankers occasionally sitting loaded, if not the intention or a legitimate requirement, will likely always be a reality.

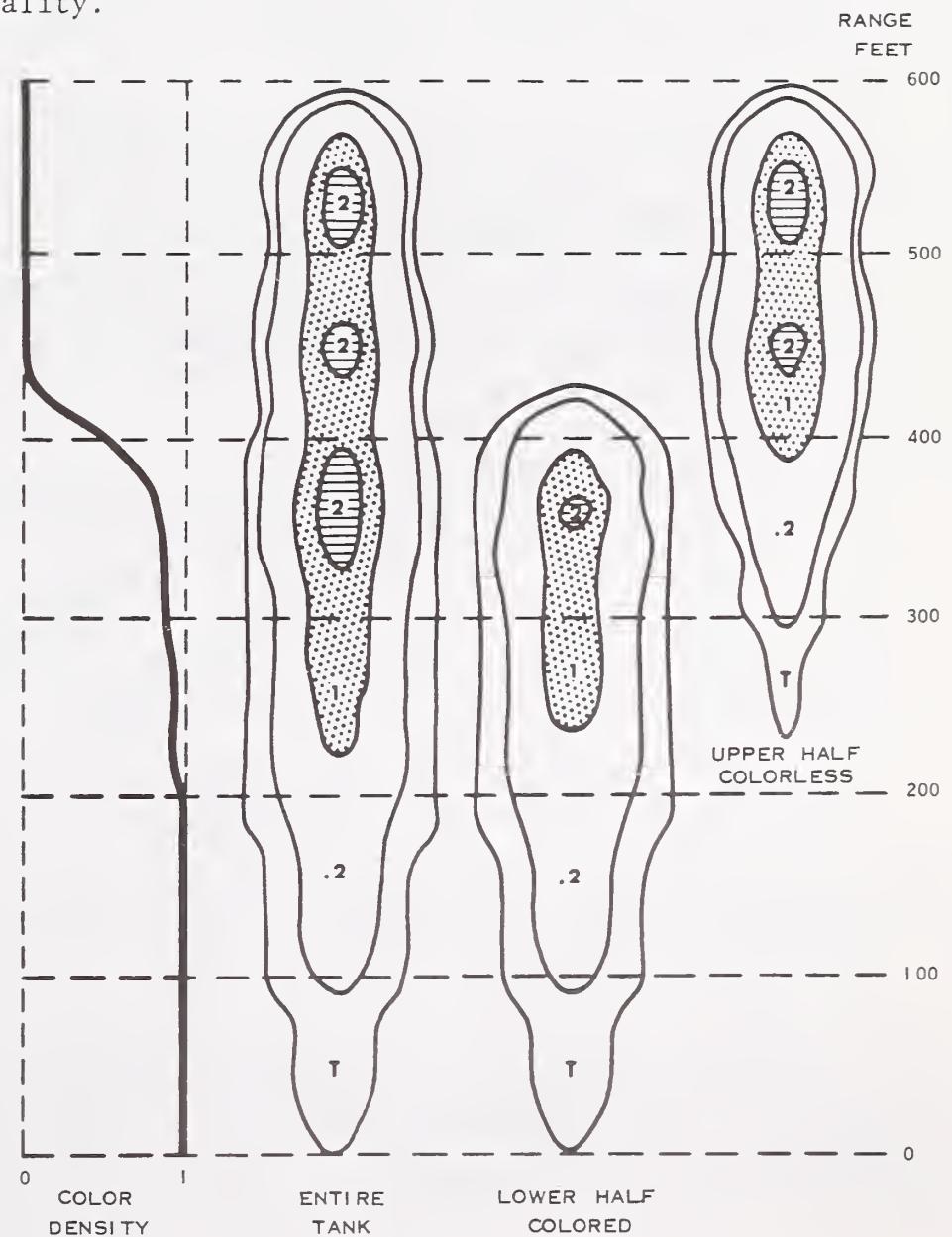


Figure 19.--The effect of retardant color separation as shown by predictions of the ground distribution patterns and color distribution of 500 gallons of retardant dropped from a B-17.

Retardant Drop Characteristics. Present specifications contain drop requirements which can be satisfied by water containing no additives. Early specifications recognized that the drop characteristics of retardants were important considerations in product qualification. However, practical standards had not been identified because thorough studies quantifying these parameters had not been conducted (a number of rather qualitative studies had been undertaken). Since these specifications were first prepared (1969) a number of drop studies have been conducted and practical requirements are now possible.

The drop data as outlined in Section 3.1.15. (Air Drop Characteristics) well illustrate differences in deliverability that result from varying retardant physical-chemical or rheological properties. Extreme differences in retardant deformation, breakup, and resulting ground distribution patterns exist between the unthickened Fire-Trol 931 and the gum-thickened Fire-Trol 931 (fig. 17 and 18). The effects of wind, aircraft speed, drop height, retardant flow rate, and load size are much less pronounced on the gum-thickened retardant than on the unthickened retardant. An explanation of these phenomena is probably best given by Andersen and others (1974a).

Thus, the use of gum-thickened retardants, tailored to specific drop and fire situations, can allow effective drops to be made from higher and safer drop heights (fig. 20)¹⁵ than considered before. Of course, there are trade-offs between accuracy and drop height which are affected by the wind conditions and type of attack (direct and indirect), but limitations will likely be determined through experience and will be subject to human abilities.

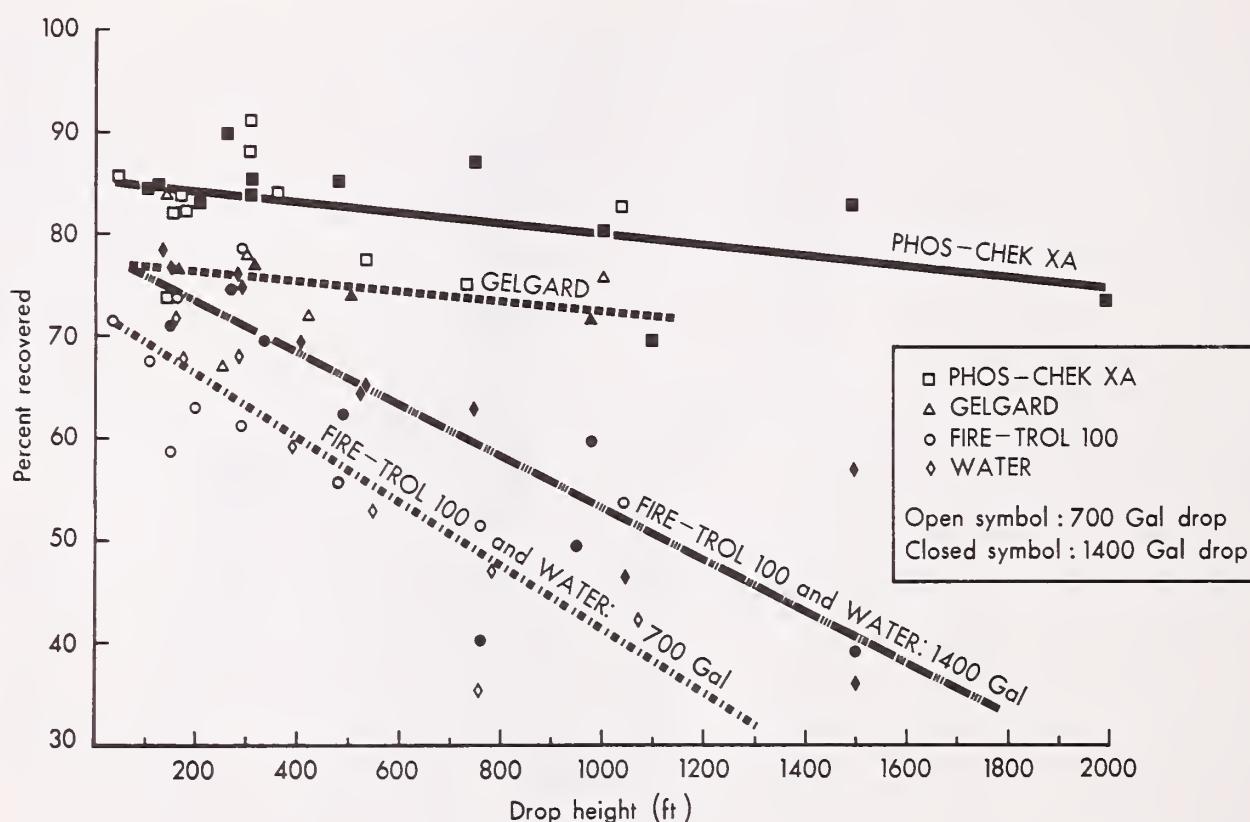


Figure 20.--The effect of type of retardant and drop height on the percent of total retardant reaching the ground.

¹⁵ Review of over 50 air tanker accidents reported to the National Transportation Safety Board during the period 1964 to 1974 indicates 55 percent of the fatalities (a total of 31 fatalities during this 11-year period) occurred from accidents during drop maneuvers. "Improving aerial delivery of chemicals through research" paper presented by C. W. George, 10-24-74, at the California-Nevada Forest Fire Council.

RECOMMENDATIONS

Based on the results of this evaluation and other studies being conducted in the area of retardant research, several recommendations regarding the use and formulation of Fire-Trol 931 APP have been made:

1. The Fire-Trol liquid ammonium polyphosphate fire retardants tested here do not meet all the specification requirements and therefore should not be used operationally in their present forms.
2. Emphasis should be placed on developing corrosion inhibitor systems for Fire-Trol 931 APP solutions which will provide corrosion protection for those alloys frequently encountered in addition to aluminum 2024-T3 and for types of corrosion encountered other than uniform and intergranular.
3. Research and development should be undertaken to improve retardant solution stability (viscosity and separation)--this may include a substitute for attapulgite clay in the liquid concentrate.
4. Gum-type thickening agents should be developed which are stable in storage (not requiring frequent circulation) and relatively insensitive to the type of APP solution, salt concentration, pH, water temperature, etc., or are otherwise adequately controllable.
5. Only those basic types of ammonium polyphosphate (10-34-0) solutions which have similar properties should be used. Use of various APP solutions resulting in different physical-chemical characteristics (corrosion, viscosity, etc.) can be adjusted for operationally only with considerable effort and supportive calibration data.
6. Mixing and handling hardware should be developed which will allow precise selections of the final retardant properties (viscosity, salt content, color) within a broad range.

PUBLICATIONS CITED

Andersen, W. H., R. E. Brown, K. G. Kato, and N. A. Louie.
1974a. Investigation of rheological properties of aerial delivered fire retardant, final report. 149 p. Shock Hydrodynamics, North Hollywood, Calif. Contract 26-3198 to IF&RES.

Andersen, W. H., R. E. Brown, and N. A. Louie.
1974b. Investigation of rheological properties of aerial delivered fire retardant. Second quarterly report, 20 p. Shock Hydrodynamics, Contract 26-3198 to IF&RES.

Andersen, W. H., R. E. Brown, N. A. Louie, and K. G. Kato.
1974c. Investigation of rheological properties of aerial delivered fire retardant. Third quarterly report, 50 p. Shock Hydrodynamics, Contract 26-3198 to IF&RES.

Blahm, Theodore H., W. C. Marshall, and G. R. Snyder.
1974. Effect of chemical fire retardants on the survival of juvenile salmonids. 44 p. Nat. Mar. Fish. Serv. Environ. Facil., Prescott, Oreg.

Davis, J. B.
1959. Air drop tests. 22 p. A report for the California Air Attack Coordinating Committee, Calif. Div. For., Sacramento, Calif.

Davis, J. B., D. L. Dibble, and C. B. Phillips.
1961. Firefighting chemicals--new weapons for the suppression crew. USDA For. Serv. Misc. Pap. 57, 27 p. Pac. Southwest For. and Range Exp. Stn., Berkeley, Calif.

Davis, J. B., D. L. Dibble, C. B. Phillips, and R. S. McBride.
1962. Viscous water and algin gel as fire control materials. USDA For. Serv. Tech. Pap. 71, 25 p. Pac. Southwest For. and Range Exp. Stn., Berkeley, Calif.

Davis, J. B., C. B. Phillips, D. L. Dibble, and L. V. Steck.
1963. Operational tests of two viscous DAP fire retardants. USDA For. Serv. Res. Note PSW-14, 11 p. Pac. Southwest For. and Range Exp. Stn., Berkeley, Calif.

Davis, J. B., and C. B. Phillips.
1965. Corrosion of air tankers by fire retardants. 38 p. A report for the California Air Attack Coordinating Committee, Calif. Div. For., Sacramento.

George, Charles W.
1971a. Retardant salt concentration measured in the field. USDA For. Serv. Res. Note INT-138, 14 p. Intermt. For. and Range Exp. Stn., Ogden, Utah.

George, Charles W.
1971b. Liquids fight forest fires. Fert. Solutions 15(6):10-11, 15, 18, 21.

George, Charles W.
1975. Fire retardant ground distribution patterns from the CL-215 air tanker. USDA For. Serv. Res. Pap. INT-165, 67 p. Intermt. For. and Range Exp. Stn., Ogden, Utah.

George, Charles W., and Ronald A. Susott.
1971. Effects of ammonium phosphate and sulfate on the pyrolysis and combustion of cellulose. USDA For. Serv. Res. Note INT-90, 27 p. Intermt. For. and Range Exp. Stn., Ogden, Utah.

George, Charles W., and Aylmer D. Blakely.
1972. Effects of ammonium sulfate and ammonium phosphate on flammability. USDA For. Serv. Res. Note INT-121, 26 p. Intermt. For. and Range Exp. Stn., Ogden, Utah.

George, Charles W., and Aylmer D. Blakely.
1973. An evaluation of the drop characteristics and ground distribution patterns of forest fire retardants. USDA For. Serv. Res. Note INT-134, 60 p. Intermt. For. and Range Exp. Stn., Ogden, Utah.

Gehring, G. A., Jr.
1974. An investigation of fire retardant caused corrosion, final report. 122 p. Ocean City Res. Corp., Ocean City, N. J., Contract 26-3250 to IF&RES.

Johansen, R. W.
1959. Monoammonium phosphate shows promise in fire retardant trials. USDA For. Serv. Res. Note 137, 2 p. Southeast. For. and Range Exp. Stn., Macon Georgia.

Johansen, R. W., and G. L. Crow.
1965. Liquid phosphate fire retardant concentrates. Fire Contr. Notes 26(2):13-16.

Operation Firestop.
1965. Progress report No. 9, aerial firefighting. 13 p. USDA For. Serv., Operation Firestop, Pac. Southwest For. and Range Exp. Stn., Berkeley, Calif.

Phillips, C. B., and H. R. Miller
1961. Testing CMC-thickened water as a fire retardant. 5 p. Fire Control Exp. 2, Calif. Div. For., Sacramento, Calif.

Pickett, Ted L.
1975. Qualification tests of fire retardant chemicals--Fire-Trol^R 931-N and Fire-Trol^R 931-P. USDA For. Serv., Equip. Dev. Cent., San Dimas, Calif.

Wood, W. C.
1970. Liquid fertilizer tested as fire retardant. Fire Control Notes 31(2):3-5.

APPENDIX A

COMPOSITION OF FIRE-TROL APP FORMULATIONS

COMPOSITION OF FIRE-TROL AMMONIUM POLYPHOSPHATE PRODUCTS

Product Identification	Composition	Percent in Concentrate
Fire-Trol 934	Allied 10-34-0 Sodium Dichromate Surfactant	96.2
Fire-Trol 930	Allied 10-34-0 Sodium Dichromate	98.5
Fire-Trol 931-A	Allied 10-34-0 Attapulgite Clay Fe_2O_3 $MgCl_2 \cdot 6H_2O$	94.1
Fire-Trol 931-B	Allied 10-34-0 Attapulgite Clay Fe_2O_3 Allied Inhibitor	88.3
Fire-Trol 931-C	Allied 10-34-0 Attapulgite Clay Fe_2O_3 Sodium Dichromate	93.5
Fire-Trol 931-D	Allied 10-34-0 Attapulgite Clay Fe_2O_3 Sodium Dichromate	93.5
Fire-Trol 931-E	Cominco 10-34-0 Attapulgite Clay Fe_2O_3 Sodium Dichromate	92.5
Fire-Trol 931-F	Stauffer 10-34-0 Attapulgite Clay Fe_2O_3 Sodium Dichromate	93.5
Fire-Trol 931-G	TVA 10-34-0 Attapulgite Clay Fe_2O_3 Sodium Thiosulfate Sodium Molybdate 2-mercaptopbenzothiazole	93.5

Fire-Trol 931-J	Allied 10-34-0 Attapulgite Clay Fe ₂ O ₃ Sodium Thiosulfate Sodium Molybdate 2-mercaptobenzothiazole	92.8
Fire-Trol 931-K	Cominco 10-34-0 Attapulgite Clay Fe ₂ O ₃ Sodium Thiosulfate Sodium Molybdate 2-mercaptobenzothiazole	92.8
Fire-Trol 931-L	Allied 10-34-0 Attapulgite Clay Fe ₂ O ₃ Dye Sodium Ferrocyanide ¹	92.9
Fire-Trol 934-L	Allied 10-34-0 Sodium Ferrocyanide	98.5
Fire-Trol 931-M	Stauffer 10-34-0 Attapulgite Clay Fe ₂ O ₃ Dye Sodium Ferrocyanide	93.0
Fire-Trol 931-N	Cominco 10-34-0 Attapulgite Clay Fe ₂ O ₃ Dye Sodium Ferrocyanide	93.0
Fire-Trol 931-P	Simplot 10-34-0 Attapulgite Clay Fe ₂ O ₃ Dye Sodium Ferrocyanide	93.0
Gum-thickened Fire-Trol 931	931-L formulation Gum-thickener	97.5-99.0
Invert emulsion thickened Fire-Trol 931	931-L formulation Petrolite invert emulsifier	95-97

¹ Patent pending for use in Ammonium Polyphosphate Fire Retardant.

APPENDIX B

RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

From

Investigation of Retardant Caused Corrosion
Final Report
Ocean City Research Corporation
USDA Forest Service Contract #26-3250, 1974

I. ABSTRACT

A program was undertaken to assess the severity of fire retardant caused corrosion on air tankers and mixing plants. A representative number of air tankers and mixing plants were inspected and comprehensive laboratory tests were conducted to identify and quantify the extent of different types of corrosion. In the laboratory tests, five fire retardants and ten alloys were investigated. The laboratory tests also included evaluation of ten protective coatings for use as maintenance coatings and evaluation of different chemicals for use as corrosion inhibitors in retardant solutions. The results of the investigation are presented with recommendations for control of fire retardant corrosion.

II. CONCLUSIONS

- A. The aerial fire retardants currently used to suppress forest fires corrode aircraft and ground mixing equipment.
- B. Corrosion of aircraft and ground mixing equipment continues to create maintenance problems.
- C. The corrosivity of fire retardants is not consistent; corrosion rates vary for each alloy depending on the particular retardant formulation.
- D. Phos-Chek XA, Fire-Trol 100, and Phos-Chek 259 are relatively non-corrosive to aluminum alloys ($\approx .1$ mil/yr by alternate immersion test).
- E. Fire-Trol 931-L is only mildly corrosive to aluminum alloys (≈ 1 mil/yr by alternate immersion test).
- F. Fire-Trol 931-D corrodes 2024-T3 aluminum, zinc, and magnesium at significant rates (>5 mil/yr by total immersion test).
- G. Fire-Trol 931-L corrodes zinc and magnesium at significant rates (>5 mil/yr by alternate immersion test).
- H. In laboratory tests, Fire-Trol 100 corrodes brass and magnesium at significant rates (>3 mil/yr by alternate immersion test). Field surveys also showed that Fire-Trol 100 corrodes steel significantly which is contrary to the results of laboratory tests.
- I. Phos-Chek 259 corrodes brass and zinc at significant rates (>5 mil/yr by alternate immersion test).
- J. Overall, Phos-Chek XA is the least corrosive of the fire retardants. It does not cause significant corrosion on any of the alloys commonly found on air tankers or in ground mixing plants.
- K. Almost all alloys will corrode excessively in uninhibited diammonium phosphate (15.0 percent solution, by weight), uninhibited ammonium sulfate (15.0 percent solution, by weight), and uninhibited ammonium polyphosphate (8.3 percent solution, P_2O_5 equivalent by weight). These chemicals should never be used as fire retardants without effective corrosion inhibitor additives.

- L. Alternate immersion conditions are significantly more corrosive to naval brass than total immersion conditions.
- M. Stainless steel alloys are virtually immune to general corrosion caused by fire retardants.
- N. Galvanic corrosion can occur at significant rates (3 mil/yr) even with the use of corrosion-inhibited retardants.
- O. The addition of corrosion inhibitors to retardant formulas can effectively reduce corrosion.
- P. Fire retardants without corrosion inhibitors are conducive to both stress corrosion and corrosion fatigue. The corrosion inhibited formulations currently in use do not completely eliminate susceptibility to stress corrosion.
- Q. The corrosivity of fire retardants can be significantly reduced by the use of additional inhibitors. Further work as follows is required to identify the most effective inhibitors:
 1. Inhibitor duration tests
 2. Stress corrosion cracking tests
 3. Corrosion rate versus inhibitor concentration tests
 4. Corrosion rate versus dilution tests
 5. Corrosion fatigue tests
 6. Inhibitor combination tests
- R. Fire retardants rapidly deteriorate many of the common maintenance coatings. Certain epoxy-base coatings will provide adequate protection as maintenance coatings.
- S. The current interim USFS specification is realistic in limiting the maximum allowable corrosion rate of 1 mil/yr on 2024-T3 aluminum. However, the specification should be expanded to include other alloys, and other types of corrosion test. Also, the test procedure should be modified to account for corrosion rate - time effects and differences that might occur under conditions of alternate immersion.

III. RECOMMENDATIONS TO CONTROL FIRE RETARDANT CORROSION

- A. Uninhibited fire retardants are quite corrosive to almost all alloys. Use only those retardant formulations containing effective corrosion inhibitor additives.
- B. Pyro causes severe corrosion on almost all alloys (except stainless steels). Pyro should never be used as a fire retardant without corrosion inhibitor additives.
- C. Most of the inhibited fire retardant now used across the country corrode aluminum alloys at an insignificant rate. However, other alloys commonly used on air tankers are susceptible to appreciable corrosion caused by exposure to fire retardant. Therefore, continuing preventative maintenance is required to control corrosion. Normal maintenance procedures as established by the Federal Aviation Administration (Advisory Circular No. 43-4 dated 5-15-73) should be followed.

- D. Fire retardants are conducive to galvanic corrosion. Where possible, avoid the following galvanic couples:
 - 1. Aluminum alloys coupled to either copper-base alloys or stainless steel alloys.
 - 2. Carbon or low alloy steels coupled to either copper-base alloys or stainless steel alloys.
 - 3. Galvanized steel coupled to aluminum, steel, copper or stainless steel alloys.
- E. Fire retardants corrode mild steel alloys sufficient to cause seizing of threaded fasteners, hinges, etc. Where seizing is a problem, substitute an austenitic Type 304 stainless steel.
- F. Fire-Trol 100 and Fire-Trol 931-L are severely corrosive to magnesium alloys. In general, avoid the use of magnesium alloys on air tankers, take particular care to prevent either of the above-mentioned retardants from contacting magnesium alloys for any appreciable time.
- G. Fire-Trol 931-L is corrosive to galvanized steel. On air tankers, do not allow Fire-Trol 931-L to contact galvanized control cables for any appreciable period of time.
- H. Vapors given off by some of the aerial fire retardants appear to be significantly corrosive. Avoid entrapment of fire retardant vapor in air tankers and storage tanks by providing proper ventilation.
- I. Fire retardants rapidly degrade most organic maintenance coatings. In mixing plant service, use amine-cured epoxy coatings for general exterior maintenance. For coating the interior of steel storage tanks, use a high build coal tar epoxy coating.

IV. RECOMMENDATIONS FOR FOREST SERVICE ACTION

- A. Initiate further studies in the following areas:
 - 1. Corrosion Inhibitors
 - 2. Vapor Zone Corrosion
 - 3. Corrosivity Variation of Liquid Ammonium Polyphosphate
 - 4. Corrosion Rate Versus Viscosity.
- B. Initiate steps to effectively transfer the technology developed in this program for implementation by air operators and retardant suppliers.
- C. Consider the acquisition of more sophisticated instrumentation that would enable more accurate determination of corrosion rates by electrochemical polarization methods.
- D. Revise and expand USFS interim specification 5100-00301 and 5100-00302a to reflect the technology developed in this program. Specific items include:
 - 1. Expand the corrosion testing to include determination of general corrosion rates not only on 2024-T3 aluminum but also 7075-T6 aluminum, naval brass, 4130 steel, and magnesium.

2. Determine corrosion rates under both total immersion conditions and alternate immersion conditions.
3. Conduct the total immersion tests over at least 30 days. Determine corrosion rates by polarization measurements on the 1st, 3rd, 7th, 14th, and 30th day in test. In addition, weigh each test specimen prior to and after the test to allow determination of corrosion rate by weight loss.
4. Conduct the alternate immersion tests over 30 days. Determine general corrosion rates by weight loss measurements.
5. Substitute double cantilever beam (DCB) type specimens for the U-bend specimens now specified to check for susceptibility to stress corrosion cracking. Include 2024-T3 aluminum and 7075-T6 aluminum in the SCC tests. The test should be total immersion for 30 days.

E. Consider modifying existing specifications on fire retardants so that corrosion inhibitor additives can be specified for different retardant solutions instead of qualifying proprietary formulas.

General Corrosion Rates (mils/yr)
Determined by Weight Loss Measurements

<u>TOTAL IMMERSION TEST (2 MONTHS)</u>										
	<u>304 SS</u>	<u>410 SS</u>	<u>BRASS</u>	<u>2024 A1</u>	<u>2024 A1C</u>	<u>6061 A1</u>	<u>7075 A1</u>	<u>4130 STEEL</u>	<u>ZINC</u>	<u>MAG</u>
Fire-Trol 931-D	.0096	.0054	.1743	7.113	1.857	.1530	2.108	.0898	23.29	>100.0
<u>ALTERNATE IMMERSION TEST (6 MONTHS)</u>										
Fire-Trol 931-L	.0026	.0097	.7800	1.363	.5419	.5038	.7664	.2563	6.383	>100.0
<u>DETERMINED BY LINEAR POLARIZATION MEASUREMENTS OVER A PERIOD OF 2 MONTHS</u>										
Fire-Trol 931-D	Initial	.0081	.1663	.1665	.1068	.1828	.1026	.0749	.0266	>100
		.0069	.1101	.1080	4.986	1.763	.8014	.8565	.0456	18.65
		.0051	.0748	.1865	5.488	1.325	.9788	1.031	.0140	2.283
		.0031	.0058	.1163	4.333	.6640	.7945	.9794	.0195	1.197
		.0010	.0014	.1108	3.080	.5517	.7822	.6659		.6921
	Final	.0064	.0043	.0871	2.263	.7676	.7377	.9389		
	Average	.0051	.0605	.1292	3.376	.6757	.6995	.7578	.0264	14.75
										>100

THE FIVE WORST GALVANIC CORROSION RATES FOR FIRE TROL 931

<u>CATHODE</u>	<u>E_c VOLTS</u>	<u>ANODE</u>	<u>E_c VOLTS</u>	<u>ΔE_c VOLTS</u>	<u>I_c $\mu a/cm^2$</u>	<u>CORROSION RATE (MIL/YR)</u>
Brass	-.10	2024 Al	-.71	.61	5.0	4.49
410 SS	-.18	2024 Al	-.71	.89	4.0	3.60
Brass	-.10	4130 St1	-.61	.51	6.5	3.02
Brass	-.10	7075 Al	-.74	.64	4.9	2.14
410 SS	+.18	4130 St1	-.61	.79	3.8	1.76

Galvanic Corrosion Rates in Selected Inhibitors

1% Ammonium Thiocyanate in Polyphosphate	Naval Brass	-.29	2024 Al	-.39	.10	.39	.35
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Average Corrosion Potentials Over 2 Month Exposure Period for Fire Trol 931

CORROSION POTENTIALS VS Ag/AgCl, VOLTS

Alloy	Naval Brass	304 SS	410 SS	Zinc	4130 St1	6061 Al	7075 Al	2024 Alc	2024 Al
Potential	-.21	+.04	-.06	-.63	-.17	-.91	-.86	-.86	-.81

Results of DCB Stress Corrosion Cracking
Tests for Inhibitor Screening Phase

<u>RETARDANT</u>	<u>INHIBITOR</u>	<u>ALLOY</u>	<u>CRACK GROWTH OVER 1000 HRS.</u>
Ammonium Polyphosphate	Ammonium Thiocyanate	2024 Aluminum	.15"

Results of DCB Stress Corrosion Cracking Tests

<u>RETARDANT</u>	<u>ALLOY</u>	<u>CRACK GROWTH</u>	<u>K_{IC}</u>	<u>K_{ISCC}</u>	<u>% REDUCTION IN K_{IC}</u>
Fire Trol 931-L	4130 St1	.976	339.0	162.9	52
Fire Trol 931-L	2024 Al	.079	132.5	121.4	6

GENERAL CORROSION RATES IN FIRE-TROL 93I-D

410 STAINLESS STEEL

304 STAINLESS STEEL

4130 STEEL

NAVAL BRASS

6061 ALUMINUM

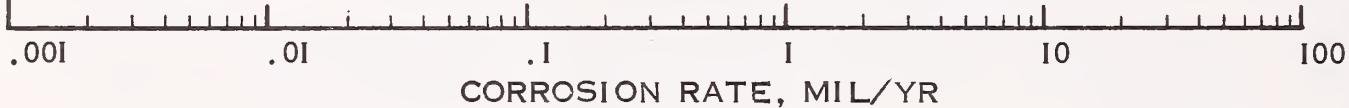
2024 ALUMINUM CLAD ALUMINUM

7075 ALUMINUM

2024 ALUMINUM

ZINC

MAGNESIUM



APPENDIX C

COMBUSTION RETARDING EFFECTIVENESS TEST DATA AND SUPERIORITY FACTORS

FLAMMABILITY DATA FOR FIRE TROL 931 L

RETARDANT	ACTIVE CHEM. P ₂ O ₅ (G/FT ²)	RATE OF SPREAD (FT/MIN)	REDUCTION IN RATE OF SPREAD (PERCENT)	RATE OF WEIGHT LOSS (G/MIN)	REDUCTION IN RATE OF WT. LOSS (PERCENT)	RESIDUE (GRAMS)	REDUCTION IN FUEL CONSUMED (PERCENT)	AVERAGE SUPERIORITY FACTOR
P. Pine								
1A	3.75	1.08	34	186	43	530	19	.325
1B	4.21	.88	46	177	46	445	10	.370
1C	3.93	.76	54	170	48	510	17	.432
2A	7.49	.50	70	127	61	615	28	.572
2B	7.11	.51	69	129	61	630	29	.571
2C	7.64	.62	62	166	49	620	28	.503
Excelsior								
1A	3.47	.88	71	187	56	245	14	.529
1B	3.47	.95	68	167	61	250	14	.527
1C	3.40	.76	75	167	61	255	14	.565
1D	3.75	.93	69	169	61	270	15	.535
2A	7.22	.54	82	126	71	395	22	.642
2B	7.53	.70	77	166	61	380	21	.596
2C	7.75	.67	78	122	71	420	23	.626
2D	8.74	.37	88	54	87	510	28	.728

FLAMMABILITY DATA FOR FIRE TROL 931 N

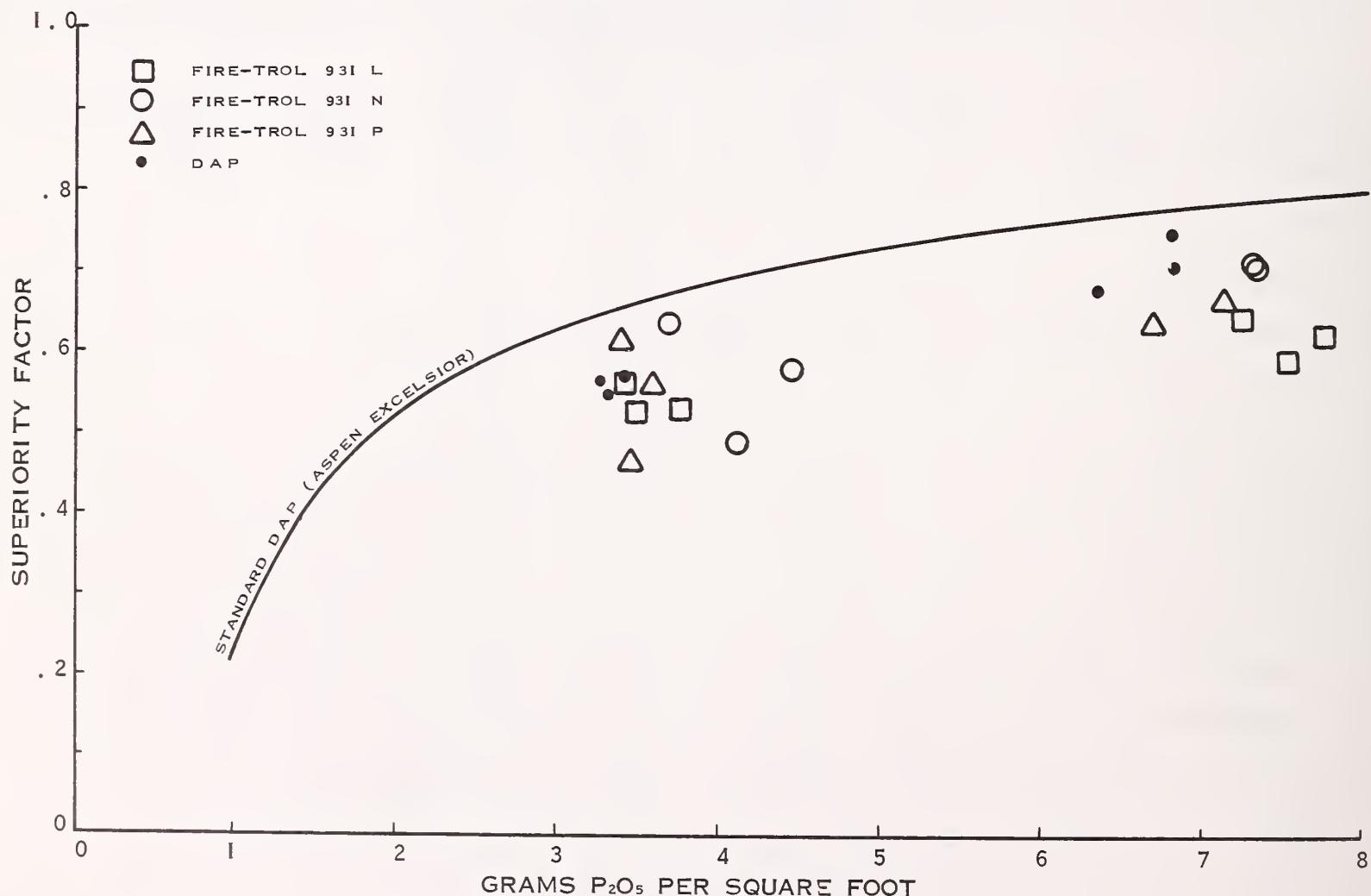
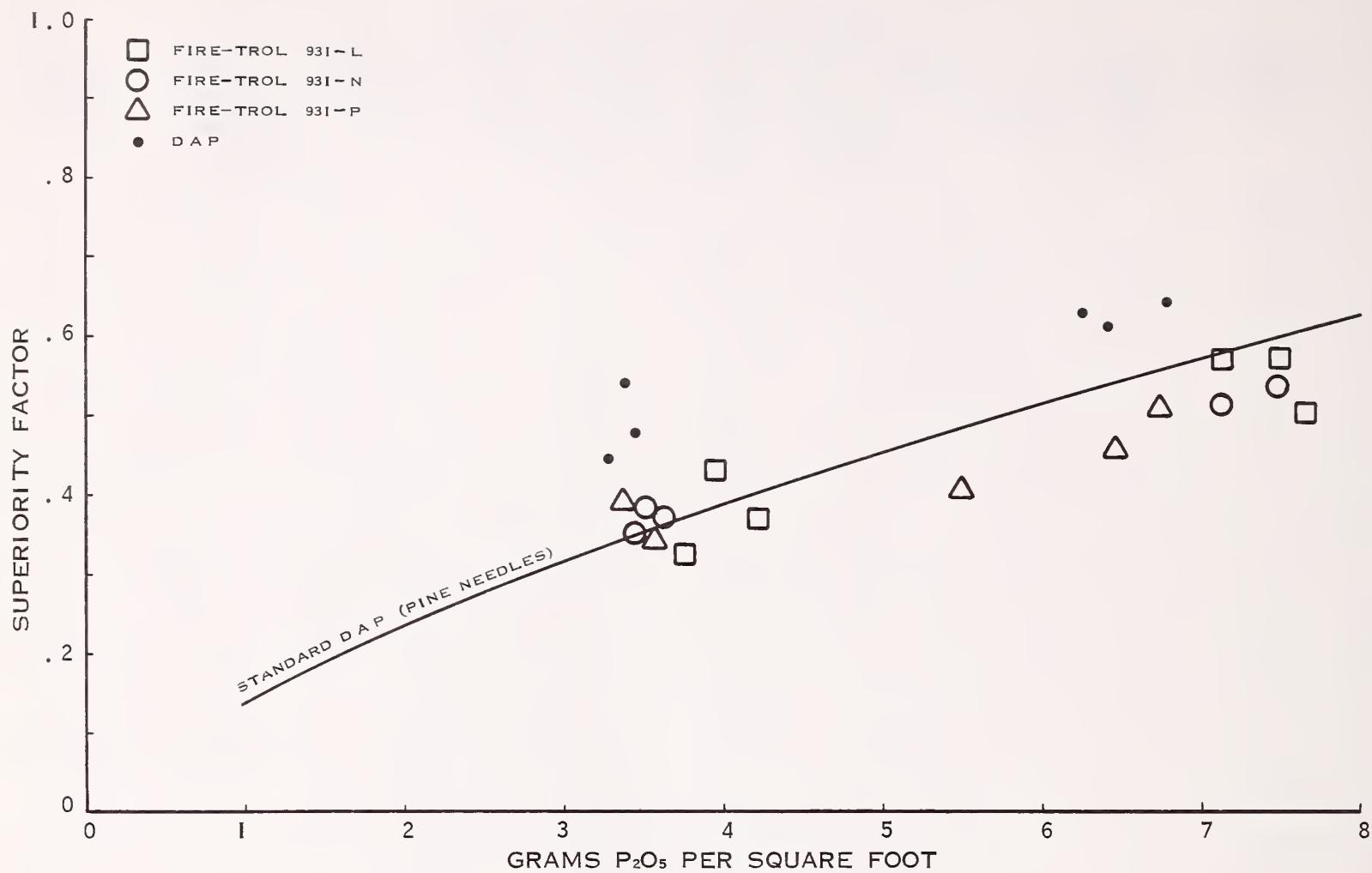
RETARDANT	ACTIVE CHEM. P ₂ O ₅ (G/FT ²)	RATE OF SPREAD (FT/MIN)	REDUCTION IN RATE OF SPREAD (PERCENT)	RATE OF WEIGHT LOSS (G/MIN)	REDUCTION IN RATE OF WT. LOSS (PERCENT)	RESIDUE (GRAMS)	REDUCTION IN FUEL CONSUMED (PERCENT)	AVERAGE SUPERIORITY FACTOR
P. Pine								
1A	3.44	1.06	34	152	54	520	18	.350
1B	3.51	.99	40	227	31	465	12	.371
1C	3.51	.86	48	187	43	490	15	.385
2A	7.69	.60	63			640	30	
2B	7.49	.56	66	152	54	625	29	.537
2C	7.12	.70	57	145	56	690	36	.514
Excelsior								
1A	3.68	.56	84	132	70	305	17	.637
1B	4.45	.80	73	124	71	280	16	.581
1C	4.11	1.07	64	203	53	280	16	.491
2A	7.32	.40	89	102	77	510	28	.708
2B	7.31	.40	89	70	84	435	24	.715
2C	7.56	.48	88			435	24	

FLAMMABILITY DATA FOR FIRE TROL 931 P

RETARDANT	ACTIVE CHEM. P ₂ O ₅ (G/FT ²)	RATE OF SPREAD (FT/MIN)	REDUCTION IN RATE OF SPREAD (PERCENT)	RATE OF WEIGHT LOSS (G/MIN)	REDUCTION IN RATE OF WT. LOSS (PERCENT)	RESIDUE (GRAMS)	REDUCTION IN FUEL CONSUMED (PERCENT)	AVERAGE SUPERIORITY FACTOR
P. Pine								
1A	3.55	.98	41	197	40	505	16	.346
1B	3.36	.98	41	147	55	530	19	.390
1C	3.52	.99	40	197	40	535	19	.349
2A	5.49	.88	46	168	49	555	22	.406
2B	6.45	.79	52	169	49	640	30	.459
2C	6.74	.63	62	158	52	607	27	.507
Excelsior								
1A	3.58	.94	73	155	65	236	13	.560
1B	3.45	1.39	60	217	51	275	15	.466
1C	3.39	.72	79	129	71	300	17	.614
1D	3.81	.85	72	197	54	197	11	.522
2A	7.10	.70	80	79	82	418	23	.663
2B	6.68	.73	79	125	72	467	26	.640
2C	7.20	.54	82	140	67	430	24	.637

SUPERIORITY FACTOR (Computed)

RETARDANT	Fire Trol 931 L	Fire Trol 931 N	Fire Trol 931 P
Number of Fires	14	10	12
Chemical in Solution			
Percent P ₂ O ₅	8.49	8.28	7.82
Density (G/ML)	1.108	1.106	1.108
Superiority Factor Equations	Y = .34523 + .03384X	Y = .28753 + .0464X	Y = .32736 + .03583X
Treatment Levels			
1 Gal/100 ft ²			
P ₂ O ₅ (G/ft ²)	3.56	3.47	3.28
Retardant S.F.	.47	.45	.45
Std. DAP S.F.	.51	.51	.49
2 Gal/100 ft ²			
P ₂ O ₅ G/ft ²	7.12	6.94	6.56
Retardant S.F.	.59	.61	.56
Std. DAP S.F.	.68	.67	.68
Mean S.F. - All Treatment			
Levels & All Fuels	.53	.53	.51



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C. W. Johnson

1977. Evaluation of liquid ammonium polyphosphate fire retardants.
USDA For. Serv. Gen. Tech. Rep. INT-41, 54 p. Intermountain
Forest and Range Experiment Station, Ogden, Utah 84401.

Summarizes the development, history, and operational use of liquid ammonium phosphate and polyphosphate fire retardants since their first use in the early 1960's. Performance of products is discussed and recommendations are made relative to meeting current Forest Service specifications and satisfying current and future operational needs.

KEYWORDS: retardant evaluation, LC, ammonium polyphosphates, liquid fire retardant, liquid fertilizer, USDA specification, LC development, corrosion, pumpability, drop patterns, separation.

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